

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

VOLUME XXVI

N^{os}. 7 and 8.

President: Prof. F. A. F. C. WENT.

Secretary: Prof. L. BOLK.

(Translated from: "Verslag van de gewone vergaderingen der Wis- en
Natuurkundige Afdeling," Vol. XXXII).

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Physics. — “*A Relation between the Spectra of Ionized Potassium and Argon.*” (Second Communication). By H. W. J. DIK and Prof. P. ZEEMAN.

(Communicated at the meeting of June 30, 1923).

The observations of the spectrum of potassium vapour under the influence of the discharge without electrodes have now been completed. These measurements go up to λ 2342,3 Å. They, too, have been made with a quartz spectrograph. We begin Table IV with 3514.0, so that Table I of our first communication¹⁾ and Table IV for a small part overlap. The values of Table IV are more accurate, and have been obtained by direct comparison with the standard iron lines.

TABLE IV. Potassium lines on discharge without electrodes.

Intensity.				λ	ν	Remarks.
EV	S	McL	D			
—	1		9	3514.0	28458	
—	—	1	9	3490.8	28647	
1	1		10	3480.9	28728	
1	1		10	3476.4	28765	
—	1		9	3468.3	28833	
—	—	—	3	3457.4	28923	
—	—	—	2	3447.8	29003	
10	2		—	3447.5		arc-line
	3		—	3446.5		arc-line
6	3		20	3439.9	29070	
1	2		15	3433.2	29128	
—	—	—	2	3427.0	29180	

¹⁾ These Proceedings, Vol. XXV, p. 67.

TABLE IV (Continued).

Intensity.				λ	ν	Remarks.
EV	S	McL	D			
1	1		15	3421.9	29223	
—	—	—		3421.0	29231	
—	—	—	1	3417.0	29266	
2	2		15	3404.2	29376	
—	1		9	3392.6	29476	
6	4		15	3384.6	29545	
6	4		15	3380.3	29583	
1	3		15	3373.5	29643	
—	6		20	3363.9	29727	
1	8			3362.5	29739	
—	2		2	3358.6	29774	
—	2		2	3356.2	29796	
8	5	6	15	3345.0	29895	
—	—	—	2	3338.0	29958	
—	—	3	2	3336.1	29975	
1	—	—	—	3326.4		
—	—	3		3324.7		
1	4	—	15	3322.2	30101	
3	4	5	15	3311.9	30194	
—	—	3	15	3301.2	30292	
3	3	5	15	3289.8	30397	
—	—	—	1	3285.5	30437	
—	3	3	10	3278.6	30501	
—	2	3	10	3261.9	30657	
—	—	3	3	3258.6	30688	
—	—	—	3	3253.9	30732	
—	—	3	—	3244.5		
—	2	—	10	3241.2	30853	
—	—	—	4	3237.8	30885	

TABLE IV (Continued).

Intensity.				λ	ν	Remarks.
EV	S	McL	D			
—	—	—	1	3226.9	30989	
1	1	1	8	3224.2	31016	
2	2	0	10	3220.2	31054	
—	1	—	3	3218.5	31071	
2	1	—	—	3217.5		
—	—	0	—	3213.0		
1	4	—	10	3209.0	31162	
—	—	4	—	3205.6		
1	3	—	10	3201.8	31232	
2	2	5	10	3190.0	31348	
—	2	—	10	3187.7	31371	
—	—	2	3	3171.8	31528	
1	1	4	9	3169.6	31550	
1	1	3	6	3157.0	31676	
—	—	2	—	3148.6		
—	—	—	1	3145.1	31795	
3	—	—	4	3142.7	31820	
4	2	4	15	3128.8	31961	
—	—	—	5	3109.7	32157	
5	4	—	15	3104.9	32208	
1	1	6	4	3102.9	32228	
1	1	2	8	3074.7	32524	
1	—	—	—	3067.3		
6	5	5	20	3061.7	32661	
1	2	0	10	3056.5	32717	
1	3	2	15	3051.9	32767	
—	—	2	3	3047.0	32819	
1	1	3	9	3030.4	32999	
1	2	3	10	3023.5	33074	

TABLE IV (Continued).

Intensity.				λ	ν	Remarks.
EV	S	McL	D			
4	3	3	15	2992.4	33418	
1	1	2	9	2986.3	33487	
—	—	2	4	2965.1	33726	
—	1	—	—	2963.4		
—	—	1	4	2954.3	33849	
—	—	—	1	2950.9	33888	
—	—	—	1	2942.9	33980	
1	1	2	10	2938.6	34030	
—	—	—	3	2927.9	34154	
—	—	1	4	2925.8	34179	
—	—	2	8	2903.4	34442	
—	—	—	1	2898.9	34495	
—	—	—	1	2893.9	34555	
—	—	—	3	2880.2	34720	
—	—	—	1	2877.5	34753	
—	—	—	2	2872.5	34813	
1	1	2	10	2854.4	35034	
—	—	—	4	2851.7	35066	
—	—	—	1	2847.7	35117	
—	—	3	2	2834.7	35277	
1	1	—	—	2833.3		
—	—	2	3	2824.3	35408	
—	—	—	3	2821.9	35437	
1	1	3	10	2819.3	35469	
—	—	—	5	2809.0	35600	
—	—	—	9	2806.3	35634	
—	—	—	5	2804.6	35656	
—	—	5	—	2803.5		
—	—	—	3	2800.3	35711	

TABLE IV (Continued).

Intensity.				λ	ν	Remarks.
EV	S	McL	D			
1	1	—	—	2780.2		
—	—	1	5	2777.9	35998	
—	—	—	1	2776.1	36022	
—	—	1	—	2768.1		
—	—	—	1	2763.4	36187	
—	1	2	9	2743.5	36450	
1	1	4	5	2736.2	36547	
—	—	1	—	2732.0		
1	1	3	9	2690.0	37175	
1	—	3	3	2662.8	37555	
—	—	1	1	2657.1	37636	
1	1	4	10	2635.1	37950	
—	—	0	—	2630.0		
1	1	2	1	2613.8	38259	
—	—	—	3	2572.4	38874	
—	—	1	—	2569.8		
—	—	—	3	2561.3	39043	
—	—	2	—	2559.2		
2	1	4	10	2550.0	39215	
—	—	—	1	2542.0	39339	
—	1	—	—	2538.7		
—	—	3	5	2536.4	39425	
—	—	—	5	2504.6	39927	
—	—	2	—	2502.4		
—	—	—	1	2485.5	40234	
—	1	3	8	2473.2	40434	
—	—	3	—	2470.4		
—	—	2	1	2452.7	40771	
—	—	—	1	2448.9	40834	

TABLE IV (*Continued*).

Intensity.				λ	ν	Remarks
EV	S	McL	D			
—	—	4	1	2447.2	40864	
1	1	2	7	2440.0	40984	
—	—	4	1	2436.7	41039	
—	—	—	2	2431.1	41134	
—	—	—	1	2415.4	41401	
—	—	—	1	2414.4	41417	
—	—	3	—	2410.4		
—	—	—	1	2404.5	41588	
—	—	3	—	2402.0		
—	—	3	—	2393.4		
—	—	—	1	2389.1	41857	
1	1	—	2	2379.2	42031	
	—	4	—	2376.3		
	—	5	2	2369.6	42202	
	—	2	—	2365.8		
	—	7	—	2362.6		
1	1	—	—	2358.9		
1	1	3	—	2350.3		
—	—	4	—	2348.3		
1	—	—	—	2344.7		
1	1	3	1	2342.3	42693	

The constant differences seem soon to stop below λ 3000. This may be in connection with the appearance of the second spark spectrum of potassium.

We have, however, also started an investigation of the lines that satisfy formulae with fourfold and ninefold RYDBERG constants. By this way the proof might be furnished that the observed spectrum belongs to once ionized potassium; besides, a quantitative comparison with the red argon spectrum may perhaps be possible.

Physics. — “*Further experiments with liquid helium. S. On the electric resistance of pure metals, etc. XII. Measurements concerning the electric resistance of indium in the temperature field of liquid helium*”. (Comm. N°. 167a from the Physical Laboratory at Leiden). By W. TUYN and Prof. H. KAMERLINGH ONNES.

(Communicated at the meeting of June 30, 1923).

§ 1. *Purpose of the investigation. Method of construction of the resistances.* For the further detection of supra-conducting metals it seems desirable to investigate the behaviour of those elements which take a place near already known supra-conductors in the periodic system. Indium — above thallium and by the side of tin — seemed a suitable metal.

The chemically pure indium (4 grammes) was supplied by E. DE HAËN, G. m. b. H.¹⁾. From wire extruded from this to a thickness of 0.1, m.m. we constructed the resistances *In*—1922—I, $W_0=4,704, \Omega$, *In*—1922—II, $W_0=3,708, \Omega$ and *In*—1922—III, $W_0=3,799, \Omega$; the resistances were, however, not enclosed in helium gas. A fourth resistance, *In*—1922—A, $W_0=4,609, \Omega$ was obtained by winding another piece of the same wire also bifilarly on a glass tube; silk thread served here for insulation²⁾. The values W_0 were determined on December 22nd 1922 in the way as described in Comm. N°. 160a.

§ 2. *Measurements in liquid helium.* The four resistances were placed in the cryostat provided with a stirring apparatus, represented in Comm. N°. 124c, fig. 4. The measurements took place by compensation of the potential at the extremities of a known and an unknown resistance connected in series, by the aid of a compensation

¹⁾ The high amount of $\left(\frac{W}{W_0}\right)_{T=4^{\circ}, 2 \text{ K.}}$ of all the resistances constructed from this made us doubt the purity of the indium supplied. On inquiry the firm told us in a letter dated March 22nd 1923 “that they had sent chemically pure indium metal, free from impurities”.

²⁾ Old indium wires are difficult to fuse together to obtain the four required extremities; treatment with HCl removes this difficulty.

apparatus free of thermo-electromotive forces by DIESSELHORST's method, supplied by O. WOLFF; the strength of the current through the resistances was 4 m.a. For the determination of the temperatures the vapour pressures of the helium-bath were measured, below 400 m.m. Hg. with the cathetometer; the corresponding temperatures were then derived by means of the formula of Comm. N°. 147b, p. 33¹⁾.

The results of the measurements follow in the tables I, II, III and IV. Near the vanishing-point, where the successive temperature

TABLE I. Indium—1922—I.

Date.	p_{helium} in m.m. Hg.	T .	$w = \left(\frac{W}{W_0}\right)_{In-1922-I}$ ²⁾
December 8, 1922	775.4	4.23 K.	0.1373 ₂
December 20, 1922	394.4 ₉	3.60	0.1372 ₃
	339.3 ₉	3.48	0.1371 ₄
	310.1 ₁	3.41	0.1370 ₈
	308.8 ₃		0.1370 ₇
	307.4 ₀		0.1367 ₈
	306.8 ₉		0.1367 ₂
	305.4 ₅		0.1364 ₀
	304.0 ₀		0.1363 ₆
	301.5 ₉		0.1359 ₇
	299.5 ₉		0.132
December 8, 1922	299.4 ₆		0.120
December 20, 1922	298.1 ₈		0.016
	295.4 ₈	3.38	0.0000 ₃
December 8, 1922	12.4 ₀	1.87	0.00000

¹⁾ This formula has been calculated out of measurements performed 1913. If by the side of these measurements one takes those of 1911 into account, and interpolates graphically, temperatures are obtained which often considerably deviate from those calculated with the formula. The vanishing-point temperature of thallium e.g., graphically derived in this way in Comm. No. 160a, is 2,°32 K; the formula gives 2,°47 K. Until the vapour pressure curve of helium is more accurately known, we give the read vapour tensions, and state also, how we have calculated the temperatures from them.

²⁾ Below the vanishing-point the measured potential differences have been recalculated to resistances, as if OHM's law were valid.

TABLE II. Indium—1922—II.

Date.	p_{helium} in m.m. Hg.	$T.$	$w = \left(\frac{W}{W_0}\right)_{In-1922-II.}$
December 20, 1922	394.3 ₇	3.60 K.	0.03392
	339.5 ₅	3.48	0.03387
	309.8 ₄	3.41	0.03387
	308.7 ₄		0.03385
	307.4 ₀		0.0202
	306.8 ₉		0.0067
	305.9 ₉		0.00000
	304.0 ₀		0.00000

TABLE III. Indium—1922—III.

Date.	p_{helium} in m.m. Hg.	$T.$	$w = \left(\frac{W}{W_0}\right)_{In-1922-III.}$
December 8, 1922	775.4	4.23 K.	0.03390
	333.7	3.46	0.03380 ₅
	310.5 ₄	3.42	0.03380 ₅
	309.0 ₅		0.03377
	307.6 ₉		0.0207
	305.9 ₀		0.0001 ₈
	304.7 ₈		0.00000
	12.4 ₀ —12.5 ₈	1.87	0.00000

TABLE IV. Indium—1922—A.

Date.	p_{helium} in m.m. Hg.	$T.$	$w = \left(\frac{W}{W_0}\right)_{In-1922-A.}$
December 20, 1922	759.7	4.21 K.	0.03420
	394.3 ₇	3.60	0.03418
	339.5 ₅	3.48	0.03415
	309.6 ₆	3.41	0.03392
	308.9 ₃		0.0297
	307.1 ₄		0.0013 ₄
	307.0 ₂		0.0001 ₄
	306.2 ₃		0.0000 ₃
	304.0 ₀		0.00000

differences are small, we give only the vapour tensions. Sometimes the resistance is given here in fewer decimals than elsewhere; the slightest change in indication of the oil-regulator described in Comm. N°. 119 is the cause that the galvanometer in the region of the great decrease of resistance does not settle down.

The tables show (cf. also fig. 1) that the rest-resistance of *In*—1922—I above its vanishing-point temperature is much greater than that of the other wires, that for *In*—1922—I the temperature at which the resistance diminishes most, has been shifted about 0,02 degree with regard to the corresponding one for *In*—1922—II and —III, and that the fall extends over a larger temperature region. Calculations with the available data by the aid of

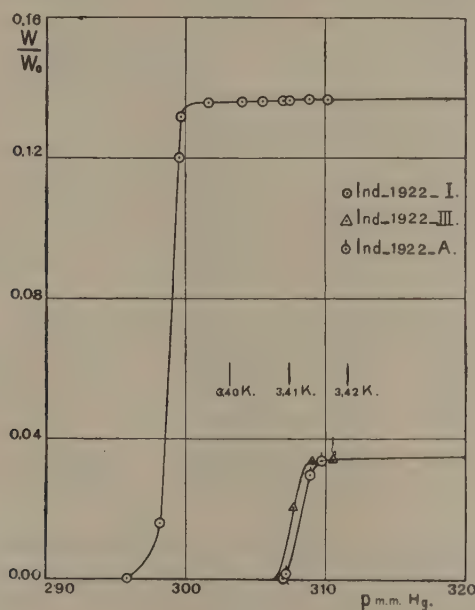


Fig. 1.

SILSBEE's hypothesis¹⁾ or by the aid of current-densities render improbable that the said displacement is caused by oxidation of *In*—1922—I throughout its length to such a degree that only a small nucleus of indium remained²⁾; the ratio of the W 's in *In*—1922—I,

¹⁾ F. B. SILSBEE. Scient. Pap. Bur. of Stand. No. 307 (1917).

²⁾ In contrast with the other wires *In*—1922—I presents a dull oxide-like surface. After the construction in July 1922 the resistance was preserved in benzine; though this was supposed to have been distilled, it seems to have contained impurities, which have attacked the wire.

—II and —III is incompatible with this¹⁾. It is improbable that the wire is strongly attacked over a small part, because then the question rises why the resistance of the better part of *In*—1922—I does not disappear at the vanishing-point temperature of the two other indium resistances. This leads to the conception that the great rest-resistance of *In*—1922—I is uniformly distributed throughout the whole wire. The equality inter se of this quantity over the three other wires makes this almost certain for them²⁾. For the

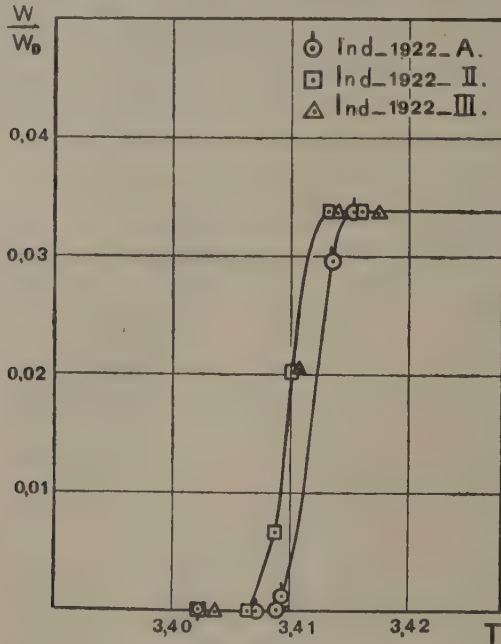


Fig. 2.

¹⁾ Measurements with *In*—1922—A on the dependence of the magnetic threshold value of the temperature yield for indium roughly a required field of 1,4 gauss for a vanishing-point displacement of 0,02 degree. i is always 4 m.a. If in agreement with SLESBEE's hypothesis the inner magnetic field of *In*—1922—I is to be 1,4 gauss larger than that of *In*—1922—II, the radius of *In*—1922—I must have been reduced to about 0,005 m.m. by oxidation, which is incompatible with the ratios of the W_0 's, when it is taken into consideration that the two resistances do not differ much in length.

The variation of the resistance with different intensities of the current has not been calculated in the experiments with indium wires. A current density 10-times greater in a tin-wire gave a vanishing-point displacement of about 0,02 degree according to Comm. 133d, table IX. With these values for indium the cross-section of *In*—1922—II would have to be 10-times that of *In*—1922—I, which also gives a wrong ratio of the W_0 's.

²⁾ The great value and equality of this rest-resistance for all three wires made us doubt the purity of the supplied indium.

present a uniform distribution of the great rest-resistance of *In*—1922—I seems strange.

It also appears from the tables (cf. also fig. 2) that there exists a difference of 0,002 degree in vanishing-point temperature between *In*—1922—A on one side, and *In*—1922—II and —III on the other side. An explanation by the assumption of differences of temperature in the helium bath seems improbable. As far as the influence of the inner magnetic field is concerned, the windings lie at a distance of 0,4 for *In*—1922—A, at a distance of 2,2 m.m. for *In*—1922—II and —III; in definite parts of cross-section and area of a winding the inner magnetic field is weakened by that of adjacent windings, and the more so as they lie more closely together. On calculation¹⁾ this weakening appears too small to be able to account for the difference found in vanishing-point temperature between *In*—1922—A and *In*—1922—II and —III.

§ 3. *The supra-conducting metals in the periodic system of the elements.* The question rises whether the vanishing-point temperature has a periodic character. In the periodic system *In* lies above *Tl*, *Sn* above *Pb*; it is remarkable that the said temperature rises both going from *In* to *Sn*, and from *Tl* to *Pb*. Towards the left, from *Tl* to *Hg*, it also ascends; if this rise continues, the vanishing-point temperature of *Au* would lie higher than of *Hg*. Since *Au* did not become supra-conducting on cooling to 1°,5 K.²⁾, the conclusion might be drawn that *Au* — perhaps with other metals — can never become so³⁾.

¹⁾ Cf. footnote 1, p. 508.

²⁾ Cf. Comm. No. 120b, § 2.

³⁾ In Comm. Suppl. No. 44, p. 35 the possibility is, on the other hand, given that the vanishing-point temperature of *Au* has not yet been reached on cooling to 1°,5 K.

Geology. — "*On the occurrence of diamond as an accessory mineral in olivine and anorthite bearing bombs, occurring in basaltic lava, ejected by the volcano Gunung Ruang (Sangir-Archipelago north of Celebes).*" By Dr. W. F. GISOEL. (Communicated by Prof. EUG. DUBOIS).

(Communicated at the meeting of June 30, 1923).

Dr. G. L. L. KEMMERLING, chief of the volcanological survey of the Dutch East Indian Archipelago, having collected some bombs out of the basaltic lavas from the volcano Gunung Ruang, composed of a mixture of a dark green to black mineral and glassy plagioclase, the latter in crystals of a size up to 1 cm., kindly intrusted those to the author for microscopical examination.

Two kinds of rock were collected; the first of these is dense and black and shows strong magnetic properties; examination with a magnifying glass reveals the presence of magnetite with a tinge of blue; under the microscope it proved to be composed of densely crowded grains of magnetite and between those one can indistinctly recognize strong pleochroitic hypersthene and green coloured monoclinic pyroxene.

The second kind, which contains much less magnetite, is composed of corroded olivine, fringed by a border of strong pleochroitic hypersthene; it also contains bottle-green monoclinic pyroxene. The plagioclase in both kinds of rock could be determined as belonging to members of the group which are very rich in anorthite.

In some of these rocks an accessory mineral occurs in a considerable number of minute grains. They may be seen most clearly in specimen 285 A in which the olivine can be recognized macroscopically; around the bomb a crust of the lava in which it is imbedded is to be seen; this lava has the composition of a basalt with bottle-green augite and very basic plagioclase.

The plagioclase is twinned according to the albite- and Carlsbad laws; one of the thin sections shows a plagioclase with three lamellae; the first shows in the conoscope, between crossed nicols, the emerging of the *Z*-axis within the field of view, slightly inclined to the surface of the section; the extinction amounts to 65 degrees. The second lamel shows in the conoscope the emerging of the *X*-axis, also

slightly inclined; the extinction is 32 degrees. The extinction of the third lamel is 85 degrees. These observations unmistakable point to a plagioclase very rich in anorthite.

The hypersthene is strongly pleochroitic from pale green to brown pink and has a double refraction rather strong for an orthorhombic pyroxene. The hypersthene often contains freakishly formed grains of magnetite.

The olivine, as seen under the microscope, is colourless; it has a high double refraction and is always corroded.

The above mentioned accessory mineral occurs in well-shaped colourless crystals, which are most like to octahedrons, occasionally with pyramids on the planes, forming triakisoctahedrons; the size of these crystals is minute, in most cases they are thinner than the section is, about $\frac{1}{70}$ mm. The slide was difficult to cut. The crystals are isotropic, they diminish the colour of polarisation of the host-crystal, but are dark with the host-crystal between crossed nicols. They show a large black border in ordinary light, also when they occur in olivine, owing to their very high refraction.

In many cases the border is so large that only a cone of light emerges at or near the centre of the grains; this cone can be followed by moving the tube up and down. The mineral in question occurs both within olivine and anorthite; in the latter it is principally deposited on the planes of zonal structure. Besides the crystals also some irregular grains occur of the same substance, showing the same properties.

The hypersthene is, remarkable enough, devoid of this mineral or contains only some occasional grains.

A fragment of the rock with a flat side was chosen; under applications of pressure striae could be obtained on topaz and on corundum. Pressure had to be applied, because in preparing the slides it became evident that the grains of the mineral were easily jerked out; consequently many cavities are to be seen in the slides.

To resume: the mineral is isotropic, has an octahedral habitus, a very high index of refraction and a hardness exceeding that of corundum, if at least we may assume that the striae on these minerals are due to the minute grains; about this however little doubt is possible. From these observations we must conclude that the mineral is diamond; no further experiment being required, which would indeed be very difficult owing to the extreme minuteness of the grains.

Assuming this to be true, it seems to me, that it throws a wonderful happy light upon the genesis of this mineral. As everywhere

else, the mother-rock has a peridotitic nature; but in this case there can be no question of layers of coal or shales, broken through by lava, fragments of which possibly could have been taken up in the lava and could be the source of the carbon in the rock.

The diamond is here a primary mineral and even older than the olivine.

The question left to be answered is this: why is the hypersthene free from grains of diamond, the olivine and anorthite containing them both? notwithstanding the fact that the hypersthene crystallized after the olivine and before the plagioclase.

The solution of this question is presumably, that the rock was originally wholly composed of olivine, and that in the cavities, formed by resorption, the anorthite crystallized; the olivine being resorbed the crystals of diamond were freed and suspended in the mother-liquor; the hypersthene has, by surface-tension, repelled these grains, which were collected in the anorthite, in which they occur as above stated, on the planes of growth or zonal structure. This being true, the reaction $\text{olivine} \rightarrow \text{hypersthene} + \text{magnetite}$ cannot have occurred in the solid phase because in that case there could have been no reason for the diamond to be driven out.

Mathematics. — "*The Complex of the Conics which cut Five Given Straight Lines.*" By Dr. G. SCHAAKE. (Communicated by Prof. HENDRIK DE VRIES).

(Communicated at the meeting of June 30, 1923).

§ 1. We can represent the conics k^2 cutting five given straight lines a_1, a_2, a_3, a_4, a_5 on the points of space by associating to each of these conics the pole K of its plane π relative to a given quadratic surface O . To any point K there corresponds the conic k^2 in the polar plane π of K passing through the points of intersection A_1, A_2, \dots, A_5 of a_1, a_2, \dots, a_5 with π .

For this representation the points of the straight lines a'_1, a'_2, \dots, a'_5 which are associated to a_1, a_2, \dots, a_5 relative to O , are singular. If we take for instance K on a'_1 , π passes through a_1 and A_1 becomes accordingly indefinite. To K there corresponds the pencil of conics k^2 passing through the points of intersection A_2, \dots, A_5 of π with a_2, \dots, a_5 . These are double conics of the system S_2 under consideration of ∞^3 individuals.

There are accordingly five straight lines a'_k of singular points of the second order. To a point of any of these straight lines there corresponds a pencil of double conics of S_2 . Each of these straight lines is the representation of a system of ∞^3 conics the planes of which pass through one of the straight lines a_k and which cut the other four of these lines.

If we choose K on one of the two straight lines t'_{11} and t'_{12} cutting the lines a'_2, a'_3, a'_4, a'_5 , e.g. on t'_{11} , π passes through the associated straight line t_{11} intersecting a_2, \dots, a_5 , and this plane contains ∞^1 degenerate conics of S_2 associated to K consisting of t_{11} and a straight line through the point of intersection A_1 of π and a_1 .

There are accordingly ten straight lines $t'_{11}, t'_{12}, \dots, t'_{51}, t'_{52}$ of singular points of the first order. To a point of any of these lines there corresponds a pencil of degenerate conics and each of these straight lines is the representation of a system of ∞^3 degenerate conics of which one straight line is fixed and the other straight lines form a bilinear congruence.

§ 2. If K describes a straight line l' , π revolves round the asso-

ciated line l and k has therefore always two points in common with l .

To a straight line l of points K there corresponds accordingly a system S_1 of ∞^1 conics each of which cuts a line l twice and the straight lines a_1, \dots, a_6 once.

Also the reverse is apparent.

If K describes a plane π , π continues to pass through the pole P of π .

A plane π is the image of a system S_2 of ∞^2 conics the planes of which pass through a point P and which cut a_1, \dots, a_6 . Inversely such a system is represented on a plane.

To the conics of S_2 passing through a definite point P , the points of a plane curve k_P lying in the polar plane π of P are associated. In order to find the order of k_P , we try to find the number of conics of S_2 through P and through a definite point Q of a_1 . The conics through P and Q intersecting a_2, a_4, a_6 , form a surface of the fourth order. For a plane through PQ contains the non-degenerate conic of this surface passing through P, Q and the points of intersection of this plane with a_2, a_4, a_6 , but also the straight line PQ which is a double line of the surface, because together with the two transversals of PQ , a_2, a_4 and a_6 , it forms two degenerate conics of the surface. As a_1 intersects this surface in four points, there pass through a point Q of a_1 four conics of the system S_2 of the conics cutting a_1, \dots, a_6 and passing through P . It follows from this that a plane through a'_1 cuts the curve k_P in four points outside a'_1 . Further k_P has a double point on a'_1 , which is associated to the double conic of S_1 lying in the plane through P and a_1 and passing through P and the points of intersection of this plane and a_2, \dots, a_6 . The two tangents to k_P at this double point are associated to the straight lines joining P to the two points in which the corresponding double conic cuts a_1 . The curve k_P is accordingly of the sixth order. This curve intersects also the ten straight lines t'_{ik} , e.g. the line t'_{11} in the point corresponding to the degenerate conic consisting of t_{11} and the transversal of a_1 and t_{11} through P .

The system of the conics of S_2 passing through a point P , is accordingly represented on a plane curve of the sixth order which has double points on a'_1, \dots, a'_6 and which cuts the ten straight lines t'_{11}, \dots, t'_{62} .

As k_P has six points in common with an arbitrary plane, six of the planes of the conics of S_1 pass through an arbitrary point.

The system S'_1 of the conics cutting a given straight line l , is represented on a surface O_l . The order of this surface, i. e. the

number of points of intersection with an arbitrary straight line m' , is equal to the number of conics of S_2' the planes of which pass through a straight line m . From the order just found for k_P there follows that through a point P of m there pass six conics of S_2 the planes of which contain m . All conics of S_2 in planes through m , consequently form a surface which has m as a sextuple straight line and which is of the eighth order, as a plane through m contains one more conic of this surface. Consequently among the conics of S_2 intersecting l , there are *eight* the planes of which pass through m and the surface O_l associated to S_2' is accordingly of the eighth order. Evidently the pencil associated to a point of any of the straight lines a_1', \dots, a_6' contains a double conic of S_2' and in S_2' there always lies one individual of the pencil of degenerate conics associated to a point of one of the straight lines t'_{11}, \dots, t'_{12} .

The system S_2' formed by the conics cutting a straight line l and a_1, \dots, a_6 , is therefore represented on a surface O_l of the eighth order, of which a_1', \dots, a_6' are double straight lines and t'_{11}, \dots, t'_{12} single straight lines. The two tangent planes at a point of one of the straight lines a' to O_l are the polar planes of the points where the double conic of S_2' corresponding to this point, intersects the straight line a associated to a' .

Finally we investigate the surface O_φ which is the image of the system S_2'' of the conics of S_2 touching a plane φ . The order of O_φ is again equal to the number of conics of S_2'' the planes of which pass through an arbitrary straight line m . The surface of the eighth order of the conics of which the planes pass through m and which cut a_1, \dots, a_6 , has in common with φ a curve k^8 of the eighth order which has a sextuple point in the point of intersection (m, φ) of m with φ . As each of the conics of this surface has in common with k^8 a pair of points lying on a straight line through (m, φ) , the number of individuals touching φ is equal to the number of tangents which can be drawn out of (m, φ) to k^8 , i.e. $8 \times 7 - 6 \times 7 = 14$. The system S_2'' contains consequently fourteen conics the planes of which pass through m and the order of O_φ is accordingly fourteen. Now S_2'' has two double conics in the pencil corresponding to a point of one of the five straight lines a' and this system has one individual in common with the pencil of degenerate conics corresponding to a point of one of the lines t' . This individual is a double conic of S_2'' . For if we take a straight line m of its plane, it counts twice among the conics of S_2'' the planes of which pass through m . The above mentioned pencil of degenerate conics splits off from the system of the conics of S_2 .

cutting m twice, so that there remains a surface of the seventh order which intersects φ along a curve k^7 with a fivefold point in (m, φ) . Instead of 14 we can now draw $7 \times 6 - 5 \times 6 = 12$ tangents out of (m, φ) to this curve. Hence a straight line m' through a point of a straight line t' has in this point two coinciding points of intersection with O_φ .

The system S' , formed by the conics of S_3 touching a plane φ , is represented on a surface O_φ of the fourteenth order of which a'_1, \dots, a'_6 are quadruple straight lines and t'_{11}, \dots, t'_{13} double lines.

§ 3. From the investigated representation we can now in the first place derive the number of conics which cut five straight lines and which fulfil a threefold condition ¹⁾.

$2 \times 2 = 4$ of the 48 points which a curve k_P has in common with a surface O , fall in each of the double points of k_P and one in each of the ten points of intersection of k_P with the straight lines t' . Accordingly the curve k_P cuts a surface O_l in eighteen points which are not singular for the representation.

There are therefore eighteen conics passing through a given point and intersecting six given straight lines.

$2 \times 4 = 8$ of the 84 points in which a curve k_P intersects a surface O_φ , lie in each of the five double points of k_P and two in each of the ten points of intersection of k_P and the lines t' . Here we have therefore 24 points of intersection that are not singular for our representation.

There are accordingly 24 conics passing through a given point, touching a given plane and intersecting five given straight lines.

Of the curve of the order 64, which two surfaces O_l have in common, each of the straight lines a' splits off four times and each of the lines t' once. There remains, accordingly, a curve of the order 34, k^{34} , which is the representation of the system of the conics in S_3 cutting two given straight lines. The conics of this system of which the planes pass through an arbitrary point, are represented on the points of intersection of k^{34} with the polar plane of this point.

There are therefore 34 conics which cut seven given straight lines and of which the planes pass through a given point.

We have found in § 2 that there are eight conics which cut six given straight lines and of which the planes pass through a likewise given straight line. Hence the system associated to k^{34} contains eight

¹⁾ Cf. SCHUBERT: „Kalkül der Abzählenden Geometrie“, p. 95.

JAN DE VRIES, These Proceedings, Vol. IV, p. 181.

double conics the planes of which pass through one of the lines a , and accordingly k^{34} has eight double points on each line a' .

Likewise the system corresponding to k^{34} contains pairs of degenerate conics of which the image points lie on one of the lines t' . For instance to points of t'_{11} there are associated the two conics consisting of t_{11} and the transversals of t_{11} , a_1 and the two directrices outside the lines a ours of the system of conics under consideration. Hence k^{34} cuts each of the lines t' in two points.

The curve k^{34} cuts a third surface O_l in 272 points. Four of these lie in each of the 40 double points of k^{34} , and 20 belong to the straight lines t . There are consequently 92 points of intersection that are not singular for the representation.

There are 92 conics intersecting eight given straight lines.

From the number of points of intersection of k^{34} with a surface O_φ that are not singular for the representation, there follows:

There are 116 conics intersecting seven given straight lines and touching a given plane.

A surface O_l and a surface O_φ have an intersection of the order 112. From this each of the straight lines a' splits off eight times and each of the lines t' twice. There remains a curve of the order 52.

There are 52 conics which cut six given straight lines, touch a given plane, and of which the planes pass through a given point.

Let us investigate the intersection of two surfaces O_φ more closely. It is of the order 196; each of the straight lines a' splits off sixteen times, each line t' four times. There remains, accordingly, a curve of the order 76, k^{76} .

There are 76 conics which cut five straight lines, touch two given planes, and the planes of which pass through a given point.

The curve k^{76} has as many double points on a'_1 as there are conics of which the planes pass through a_1 , which cut a_2, \dots, a_6 , and which touch the planes φ_1 and φ_2 . In order to find this number we remark in the first place that the conics through two points A and B of a_1 intersecting a_2 and touching φ_1 and φ_2 , form a surface of the eighth order. For in each plane through a_1 there lie four conics satisfying these conditions, and a_1 is not a component part of any such a degenerate conic. Hence eight conics intersecting a_2 and a_1 and touching φ_1 and φ_2 pass through A and B and the line a_1 is an eightfold straight line of the surface formed by the conics through A intersecting a_1 outside A , cutting a_2 and a_1 , and touching φ_1 and φ_2 . This surface is of the sixteenth order as appears from its intersection with a plane through a_1 . a_1 is therefore a sixteenfold straight line of the surface consisting of the conics the

planes of which pass through a_1 , which cut a_1 , a_2 and a_3 , and which touch φ_1 and φ_2 , and this surface is of the 24th order. The number of conics in question is therefore 24, and k^{76} has 24 double points on each of the lines a' . As for instance the line t_{11} is not a component part of any degenerate conic cutting a_1, \dots, a_6 and touching φ_1 and φ_2 , k^{76} has no point in common with any of the lines t' .

If we now determine the numbers of points of intersection of k^{76} with surfaces O_l and O_φ that are not singular for the representation, we find resp.:

There are 128 conics intersecting six given straight lines and touching two given planes.

There are 104 conics intersecting five given straight lines and touching three given planes.

§ 4. The genus of the system of conics through a given point P intersecting a_1, \dots, a_6 , is equal to that of the associated curve k_P , which is of the sixth order and has five double points; consequently it is *five*. According to the first theorem of § 3 these conics form a surface of the eighteenth order, Ω^{18} . To a conic of Ω^{18} we associate the two points in which it intersects a plane φ which therefore always belong to the curve k^{18} along which Ω^{18} is cut by φ . To the (1,2)-correspondence between the conics of Ω^{18} and the points of k^{18} arising in this way, we apply the formula of ZEUTHEN:

$$\eta_1 - \eta_2 = 2a_1(p_1 - 1) - 2a_2(p_2 - 1). \quad \dots \quad (1)$$

In this case $a_1 = 1$, $a_2 = 2$, $p_1 = 5$, $\eta_1 = 0$ and $\eta_2 =$ the number of conics of Ω^{18} touching φ , that is, according to § 3, 24. By substituting these values in (1) we find that p_2 , i. e. the genus of k^{18} , is equal to 21. Hence the curve k^{18} has 115 double points. Among these each of the points of intersection of φ with a line a in which k^{18} has quadruple points, must be counted six times. Further there belong to them the ten points of intersection of φ with the five double conics of Ω^{18} of which the planes pass through one of the lines a , and the ten points where φ is cut by the double straight lines of Ω^{18} i. e. the transversals t_P of two of the lines a which pass through P and form a conic of Ω^{18} together with the two transversals of t_P and the three remaining lines a . There remain accordingly 65 double points.

The surface of the conics through a given point which cut five straight lines, has a double curve of the 65th order.

A plane φ through a_1 has in common with Ω^{18} besides a_1 a

curve of the order 14, k^{14} , the points of which may be associated univalently to the conics of Ω^{18} passing through them, so that k^{14} has the genus *five* and accordingly $\frac{13 \times 12}{2} - 5 = 73$ double points.

Six of them lie in each of the four points of intersection of q with one of the lines a_2, \dots, a_6 and also there belong to them the four points of intersection outside a_1 of q with the double conics of Ω^{18} the planes of which do not pass through a_1 , and the points of intersection of q with the six transversals through P of two of the lines a_2, \dots, a_6 . Besides these there are 39 more double points. Hence the double curve of Ω^{18} cuts the line a_1 in 26 points. These are points of a_1 through which there pass two conics of our system that have there a common tangent plane through a_1 .

The surface Ω^{18} has a twelfold point in P , as according to § 2 our system contains six conics that cut a straight line through P outside P . A plane through P intersects Ω^{18} in a curve of the order eighteen and the genus five as again the points of this curve may be associated univalently to the conics through them. This curve has consequently 131 double points. 66 of them lie in P , six in each of the points of intersection with the lines a , and also the points of intersection outside P of the five double conics with the plane must be counted. There remain accordingly 30 double points.

The double curve of Ω^{18} cuts each line a in 26 points and has in P a 35-fold point.

To the 35 branches of the double curve through P there correspond as many pairs of conics of Ω^{18} touching each other at this point. Outside P and a_1 it must have four more points in common with the plane (P, a_1) . These lie in the points of intersection outside P of the double conic in the plane (P, a_1) and the two straight lines joining P to the points where the transversals of a_2, \dots, a_6 cut the plane. For these two points of intersection are double points of the curve under consideration.

Analogously we can examine the double curves of the surface Ω^{14} consisting of the conics that cut six given straight lines and the planes of which pass through a given point, and of the surface Ω^{12} formed by the conics that cut five given straight lines, touch a given plane, and the planes of which pass through a given point.

§ 5. We shall first determine the genus of the curve k^{14} belonging to the intersection of two surfaces O_l and O'_l . The cone K^{14} projecting k^{14} out of an arbitrary point K , has in common with O_l

besides k^{34} a curve of the order 238, k^{238} . This curve has double points in each of the double points of k^{34} , because the entire intersection of K^{34} and O_l has a quadruple point in such a point. Further K^{34} cuts each of the lines α' in 18 more points and here k^{238} has double points. But this curve has 32 single points on each of the lines l' .

The surface O_l' is cut by k^{238} in

$$238 \times 8 - 5 \times 26 \times 4 - 10 \times 32 = 1064$$

points that are not singular for the representation. These are points of intersection of k^{34} and k^{238} ; a part of them lie in the points where a generatrix of K^{34} touches the surface O_l , hence in the points of intersection of k^{34} with the polar plane of K relative to O_l that are not singular for the representation. As this polar surface is of the order seven and passes singly through the lines α' , it cuts k^{34} in $7 \times 34 - 5 \times 2 \times 8 = 158$ non-singular points. The remaining 906 points of intersection of k^{34} and k^{238} are the points where the bisecants of k^{34} through K cut this curve. Hence there pass 453

bisecants of k^{34} through K , and in a plane there lie $\frac{34 \times 33}{2} = 561$

bisecants of this curve.

Accordingly:

The bitangents of the developable surface that is enveloped by the planes of the conics intersecting seven given straight lines, form a congruence (561, 453).

As K^{34} has $453 + 5 \times 8 = 493$ double generatrices, the genus of the curve k^{34} , hence also the genus of the system of the conics cutting the lines $\alpha_1, \dots, \alpha_5, l$ and l' , is equal to: $16 \times 33 - 493 = 35$.

To each conic of the surface Ω^{32} corresponding to the curve k^{34} , we associate again the pair of points in which such a conic cuts an arbitrary plane φ ; it belongs to the curve k^{32} along which Ω^{32} intersects the plane φ . We apply the formula:

$$\eta_2 - \eta_1 = 2\alpha_1(p_2 - 1) - 2\alpha_2(p_1 - 1) \quad . \quad . \quad . \quad (1)$$

to the correspondence (1,2) arising in this way between the conics of Ω^{32} and the points of k^{32} . Here η_2 = the number of conics cutting seven straight lines and touching a plane; according to § 3 it is 116. Further $\eta_1 = 0$, $\alpha_1 = 1$, $\alpha_2 = 2$ and $p_1 = 35$. By the aid of these values there follows from (1) that the genus of k^{32} is equal to 127.

The number of double points of k^{32} is consequently $91 \times 45 - 127 = 3968$. As there pass eighteen conics of Ω^{32} through a point of one of the directrices of this surface, whence these directrices are

eighteenfold straight lines of Ω^{92} , k^{92} has eighteenfold points in the points of intersection of φ with these directrices and each of these points contains $\frac{18 \times 17}{1 \times 2} = 153$ out of the number of double points.

The points of intersection of φ with the 70 double straight lines of Ω^{92} , i.e. the transversals d of four of the directrices, each of which forms a pair of two degenerate conics of Ω^{92} together with the transversals of d and the three remaining directrices, are double points of Ω^{92} , just as the 112 points of intersection of φ with the $7 \times 8 = 56$ double conics of k^{92} the planes of which pass through one of the directrices. There remain accordingly 2715 double points.

The surface formed by the conics intersecting seven given straight lines, has therefore also a double curve of the order 2715.

The intersection of Ω^{92} with a plane φ through a_1 , consists besides of a_1 of a curve of the order 74, k^{74} . If we associate to a point of k^{74} the conic of Ω^{92} passing through it, there arises a (1,1)-correspondence between the conics of Ω^{92} and the points of k^{74} . The genus of k^{74} is accordingly 35 and the number of double points $73 \times 36 - 35 = 2593$. The points of intersection of φ and the six directrices of Ω^{92} outside a_1 are eighteenfold points of k^{74} , and each of them is therefore contained 153 times in the said number of double points. Also each intersection of φ with one of the thirty double straight lines of Ω^{92} that do not cut a_1 , and each point of intersection outside a_1 of φ and one of the 48 double conics of Ω^{92} that cut a_1 only once, is a double point of k^{74} . There remain therefore 1597 double points. Hence:

The double curve of Ω^{92} cuts each of the directrices of this surface in 1118 points. These are points through which there pass two conics of our system that have there a common tangent plane through the directrix.

Analogously it is possible to examine the double curves of the surface Ω^{116} formed by the conics intersecting six given straight lines of the touching a given plane, and of the surface Ω^{128} consisting of lines and conics intersecting five given straight lines and touching two given planes.

Mathematics. — “On the Plane Pencils Containing Three Straight Lines of a given Algebraical Congruence of Rays”. By Dr. G. SCHAAKE. (Communicated by Prof. HENDRIK DE VRIES).

(Communicated at the meeting of June 30, 1923).

§ 1. In his „*Kalkül der Abzählenden Geometrie*”, p. 331, SCHUBERT finds that the vertices of the plane pencils containing three straight lines of the congruence which two complexes of rays of the orders m and m' have in common, form a surface of the order:

$$\frac{1}{3} mm' (mm' - 2) (2mm' - 3m - 3m' + 4),$$

and the planes of these pencils envelop a surface of the same class. In this paper we shall examine what these results become for an arbitrary algebraic congruence of rays. With a view to this we make use of the representation of a special linear complex C on a linear three-dimensional space R_3 which is described in STURM: „*Liniengeometrie*”, I, on p. 269. First, however, we shall give a derivation of this representation which differs from the one l. c.

§ 2. If we associate to a straight line l with coordinates p_1, \dots, p_6 the point P in a linear five-dimensional space R of which the six above mentioned quantities are the homogeneous coordinates, a special linear complex C is represented on the intersection of a variety V with the equation

$$p_1 p_4 + p_2 p_5 + p_3 p_6 = 0$$

and one of its four-dimensional tangent spaces R_4 .

This intersection is a quadratic hypercone K that has its vertex T in the point where R touches the variety V . As the generatrices of K intersect an arbitrary three-dimensional space in the points of a quadratic surface, K contains two systems of planes each of which projects one of the scrolls of the surface in question out of T . Two planes of the same system have only the vertex T in common, two planes of different systems a generatrix of K . The planes V_p of one system are the representation of the stars of rays of the complex C , which have therefore their vertices on the axis a of C , and the fields of C the planes of which pass through a , are associated to the planes V_v of the other system. The axis a of C and the

plane pencils of this complex containing α , correspond resp. to the vertex T of K and the generatrices of this hypercone. A straight line of K in a plane V_p represents a plane pencil of C the vertex of which lies on α , and a plane pencil of C of which the plane passes through α , is associated to a straight line of a plane V_m .

Now we assume on K a point S and in the four-dimensional space R_4 a three-dimensional space R_3 . The representation mentioned in § 1 arises, when we associate to each straight line l the projection L of P out of S on R_3 , if P is the point on K corresponding to l .¹⁾

§ 3. The straight line s of C of which S is the image point on K , is a *singular straight line* of the second order for the correspondence ($l-L$). For all the points of the plane ϱ that the three-dimensional tangent space R of K at S , lying in R_4 , has in common with R_3 , are associated in R_3 to this straight line.

In R there lie the two planes V_p^1 and V_v^1 of K of which the intersection is the generatrix b_1 of K through S . To these planes there correspond resp. the star of C , that has its vertex in the point of intersection A of s and α , and the field of C consisting of the rays of the plane α that passes through s and α . The star A and the field α have in common the plane pencil (A, α) to which the straight line b_1 on K is associated.

The planes V_p^1 and V_v^1 cut ϱ resp. along the straight lines p_1 and v_1 , each consisting of points that are singular for the correspondence ($l-L$). For to each point L of p_1 there corresponds on K a straight line of V_p^1 through S , hence in C a plane pencil containing s , with vertex in A . Likewise a plane pencil in α containing s , is associated to each point L of v_1 . The point of intersection B_1 of p_1 and v_1 is the image point L for all rays l of the plane pencil (A, α) . In this way the ∞^2 straight lines of the star A correspond to the ∞^1 points of p_1 , the ∞^2 rays of the field α to the ∞^1 points of v_1 .

To a plane pencil with vertex on α a straight line on K in a plane V_p , which accordingly intersects V_m , is associated; consequently to such a plane pencil in R_4 corresponds a straight line cutting v_1 . Inversely the plane through S and a straight line of R_4 cutting v_1 , intersects the hypercone K along a straight line in V_m through S , to which there corresponds the plane pencil of C that is associated

¹⁾ The method applied here, has been indicated for the rays of space by FELIX KLEIN. Cf. Mathem. Annalen, Bd. 5, p. 257.

to the singular point of intersection of the chosen straight line with v_1 , and along a straight line cutting V_{v_1} , which lies therefore in a plane V_p and corresponds to a plane pencil of C the vertex of which lies on α . In the same way it is evident that the pencils of C in planes through α , are represented on the straight lines of R_1 which cut p_1 , and that the plane pencils containing α are associated to the straight lines through the point of intersection B_1 of p_1 and v_1 (for a plane through SB_1 cuts the hypercone K outside SB_1 along a generatrix).

To a star of C , the vertex of which lies consequently on α , there corresponds on K a plane V_p that cuts V_{v_1} along a straight line and the projection of which on R_1 passes accordingly through v_1 . Hence a plane through v_1 is associated to a star of C in R_1 . It is easily seen that also the reverse holds good and that the fields of C , the planes of which pass through α , are represented on the planes of R_1 through p_1 .

§ 4. A congruence $\Gamma(\alpha, \beta)$ of the order α and the class β has in common with C a scroll Ω of the order $\alpha + \beta$ that has α as an α -fold directrix. If further Γ has the rank r , there are r plane pencils through α containing two straight lines of Ω .

The curve γ in R_1 on which Ω is represented, cuts p_1 in the α points that are associated to the α generatrices of Ω which pass through A , and v_1 in the β points that correspond to the β generatrices of Ω in the plane (α, s) . A plane through p_1 cuts γ outside p_1 in the β image points of the straight lines which the corresponding field of C has in common with Ω , and it appears in the same way that a plane through v_1 intersects the curve γ outside v_1 in α points. Hence the order of γ is $\alpha + \beta$.

To the r plane pencils through α that contain two straight lines of Ω , there correspond in R_1 as many bisecants of the curve γ through B_1 . Besides the lines p_1 and v_1 which cut γ resp. α and β times pass through B_1 . The number of apparent double points of γ is accordingly:

$$r + \frac{1}{2} \alpha (\alpha - 1) + \frac{1}{2} \beta (\beta - 1).$$

We shall just mention an application that STURM gives on p. 271 of his book quoted in § 1. The order of the focal surface of the congruence Γ is equal to the number of sheaves with vertices on α containing two straight lines of Γ , hence also of Ω , that are infinitely near to each other. These are represented on the planes through v_1 touching γ outside v_1 . Hence the order of the focal surface of Γ is equal to the number of points of intersection outside γ of v_1 with

the surface of the tangents of γ . The order of the latter surface, that has γ as a double curve (cuspidal curve), is equal to

$$2(\alpha\beta-r).$$

We find this by substituting in the formula $n(n-1)-2h$ for n the order $\alpha+\beta$ of γ and for h the above mentioned number of apparent double points of this curve. As v_1 cuts the surface under consideration on the double curve γ in β points, we find for the number of points of intersection outside γ , i. e. the order of the focal surface of the congruence I :

$$2\beta(\alpha-1)-2r.$$

The class of the focal surface of I is equal to the number of planes through a containing two straight lines of I , hence also of Ω , that are infinitely near to each other, or equal to the number of planes through p_1 touching γ outside p_1 . As p_1 cuts the curve γ in α points, we find for the class in question:

$$2\alpha(\beta-1)-2r.$$

§ 5. In order to find the order of the surface formed by the vertices of the plane pencils containing three generatrices of I , we try to find the number of these plane pencils that have their vertices on a . These belong to C and are represented on the trisecants of γ that cut v_1 outside this curve.

The order of the surface Δ of the trisecants of γ is found by substituting in the formula:

$$(n-2)\{h-\frac{1}{6}n(n-1)\},$$

given by CAYLEY, for n the order $\alpha+\beta$ of γ and for h the number of apparent double points of this curve found in § 3. We find in this case:

$$(\alpha+\beta-2)\{r+\frac{1}{2}\alpha(\alpha-1)+\frac{1}{2}\beta(\beta-1)-\frac{1}{6}(\alpha+\beta)(\alpha+\beta-1)\}$$

or, after a simple reduction:

$$(\alpha+\beta-2)r+\frac{1}{3}\alpha(\alpha-1)(\alpha-2)+\frac{1}{3}\beta(\beta-1)(\beta-2).$$

In order to find the number of generatrices of Δ that cut v_1 , we remark that these are the common straight lines of Δ and the special linear complex that has v_1 as axis. Now the axis of a special linear complex C may be considered as a double line of C . This follows in the first place from the representation of C on a hypercone K that has been described in § 2 and through which the axis of C is transformed into the vertex of K , but also from the well known property that $n-2$ generatrices of a scroll of the order n cut a straight line of this scroll. As further v_1 has β points in common

with γ , it is apparently a $\frac{\beta(\beta-1)(\beta-2)}{6}$ -fold generatrix of \mathcal{A} . The number of generatrices of \mathcal{A} cutting v_1 , is therefore found by diminishing the order-number found above, by:

$$\frac{1}{3} \beta (\beta-1) (\beta-2).$$

Hence there are

$$(\alpha + \beta - 2) r + \frac{1}{3} \alpha (\alpha-1) (\alpha-2)$$

straight lines of \mathcal{A} which cut v_1 .

In the first place the straight line p_1 must be counted $\frac{\alpha(\alpha-1)(\alpha-2)}{6}$ times, for as this line has β points in common with γ it is an $\frac{\alpha(\alpha-1)(\alpha-2)}{6}$ -fold generatrix of \mathcal{A} . Further the number found above

has to be diminished by the number of trisecants of γ that cut v_1 on γ . This is the case in each of the β points that γ has in common with v_1 . We find the number of trisecants of γ passing through such a point, by the aid of the property that through a point of a twisted curve of the order n with h apparent double points, there pass $h-n+2$ straight lines that contain two more points of the curve, if we take into account that in our case for each of the said β points v_1 counts $\frac{(\beta-1)(\beta-2)}{2}$ times among the trisecants of γ

passing through them, as v_1 contains $\beta-1$ more points of γ outside the point under consideration. Consequently

$$\beta \left\{ r + \frac{1}{2} \alpha (\alpha-1) + \frac{1}{2} \beta (\beta-1) - \alpha - \beta + 2 - \frac{1}{2} (\beta-1) (\beta-2) \right\}$$

or

$$\beta \left\{ r + \frac{1}{2} \alpha (\alpha-1) (\alpha-2) \right\}$$

trisecants of γ that cut v_1 on γ , must be taken apart.

If we subtract these two numbers of straight lines from the aforesaid number of straight lines of \mathcal{A} that cut v_1 , we find that

$$\frac{1}{3} (\alpha-2) \{ 6r - (\alpha-1) (3\beta-1) \}$$

trisecants of γ intersect v_1 outside this curve.

According to the beginning of this § we arrive at the following theorem:

The locus of the vertices of the plane pencils that have three straight lines in common with a congruence $\{\alpha, \beta\}$ of the rank r , is a surface of the order:

$$\frac{1}{3} (\alpha-2) \{ 6r - (\alpha-1) (3\beta-\alpha) \}.$$

§ 6. In order to show that the result found in § 5, is in accordance with the result of SCHUBERT, mentioned in § 1, we have to know the rank of the congruence $\Gamma(mm', mm')$ that two complexes C_1 and C_2 of the orders m and m' have in common. It might suffice to refer to SCHUBERT, *Kalkül der Abzählenden Geometrie*, where there is found on p. 330 a derivation of this number. We shall however show that the order of Γ may also be found by the aid of the representation used in this paper.

The surface Ω consisting of the straight lines of Γ which cut the axis a of C_1 is of the order $2mm'$ and has a as an mm' -fold straight line. It is the intersection of the two congruences $\Sigma_1(m, m)$ and $\Sigma_2(m', m')$ consisting of the straight lines out of C_1 and C_2 that cut a .

Σ_1 and Σ_2 are represented resp. on two surfaces S_1 and S_2 in R_3 . As C_1 , hence also Σ_1 , contains m generatrices of an arbitrary plane pencil of C_1 , all points of p_1 and v_1 are m -fold points of S_1 and all straight lines cutting p_1 and v_1 have m more points in common with S_1 . S_1 has accordingly the order $2m$ and p_1 and v_1 are m -fold straight lines of S_1 . In the same way S_2 has the order $2m'$ and p_1 and v_1 are m' -fold straight lines of this surface. The intersection of S_1 and S_2 consists of the straight lines p_1 and v_1 , each counted mm' times, and the curve γ on which Ω is represented. This curve has the order $2mm'$ and has mm' points in common with each of the straight lines p_1 and v_1 . We first determine the number of apparent double points of γ .

The cone A projecting γ out of an arbitrary point L of R_3 , is of the order $2mm'$ and has in common with S_1 besides γ a curve ϱ of the order $4m^2m' - 2mm' = 2mm'(2m - 1)$. The curve ϱ has $(m - 1)$ -fold points in the $2mm'$ points where γ cuts the lines p_1 or v_1 , because the entire intersection of A and S_1 must have there m -fold points. Further A cuts each of the lines p_1 and v_1 in mm' more points, that are m -fold points for ϱ . As all these points are m' -fold for S_2 , ϱ has $4mm'^2(2m - 1) - 2mm'^2(m - 1) - 2m^2m'^2 = 2mm'^2(2m - 1)$ points of intersection with S_2 outside p_1 and v_1 . These belong to γ and lie partly in the points where a generatrix of A touches the surfaces S_1 on γ , hence in the points of intersection with γ outside p_1 and v_1 of the first polar surface of L relative to S_1 . As this polar surface is of the order $2m - 1$ and has $(m - 1)$ -fold straight lines in p_1 and v_1 , it cuts γ outside p_1 and v_1 in $2mm'(2m - 1) - 2mm'(m - 1) = 2m^2m'$ points. The remaining $2mm'^2(2m - 1) - 2m^2m' = 2mm'(2mm' - m - m')$ points where ϱ and γ cut each other outside p_1 and v_1 , are points that the bisecants of γ through L have

in common with this curve. The number of apparent double points of γ is therefore equal to $mm'(2mm'-m-m')$.

If we choose L in the point of intersection B_1 of p_1 and v_1 , $\frac{mm'(mm'-1)}{2}$ of the chords of γ through this point coincide with each of the lines p_1 and v_1 . Through B_1 there pass accordingly $mm'(m-1)(m'-1)$ bisecants of γ different from p_1 and v_1 . According to § 3 these are the representation of as many plane pencils through a containing two straight lines of Ω , hence also of Γ . *The rank of the congruence Γ that two complexes of the orders m and m' have in common, is therefore equal to $mm'(m-1)(m'-1)$.*

If we substitute this number for r in the expression found in § 5, and if we make α and β equal to mm' , we find indeed that the order of the surface formed by the vertices of the plane pencils containing three straight lines of the intersection of two complexes of rays of the orders m and m' , is equal to:

$$\frac{1}{3} mm' (mm'-2) (2mm'-3m-3m' + 4).$$

We get another check through the application of our formula to the congruence consisting of the straight lines passing through one of n given points. For this congruence $\alpha = n$ and $\beta = r = 0$. The locus of the vertices of the plane pencils which three straight lines have in common with this congruence, consists of the planes that may be passed through each triple of the given points. By the said substitutions in the formula of § 5, we find indeed the number of these planes, namely:

$$\frac{1}{6} n (n-1) (n-2).$$

To the theorem derived in § 5 there corresponds dually:

The planes of the plane pencils that have three straight lines in common with a congruence $\{\alpha, \beta\}$ of the rank r , envelop a surface of the class:

$$\frac{1}{6} (\beta-2) \{6r-(\beta-1) (3\alpha-\beta)\}.$$

Physics. — “*Transients of Magnetic Field in Supra-conductors*”.

By G. BREIT. National Research Fellow U. S. A. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of June 30, 1923).

It is known that supra-conductivity is determined not only by temperature but also by the magnetic field and the current density ¹⁾).

In view of the considerations of SILSBEE and LANGEVIN it is probable that the only essential factors are the magnetic field and the temperature ²⁾).

This hypothesis will be adhered to below. The problems to be discussed are the calculations of the manner in which a strong magnetic field impressed from the outside on a supra-conductor destroys its supra-conductivity and the way in which the supra-conductivity is reestablished when the magnetic field is withdrawn.

If the view proposed by BRIDGMAN ³⁾ is correct there is an evolution or an absorption of heat whenever a change in the conductive state takes place. These phenomena being of unknown magnitude, they will be disregarded below. If experiments should fail to confirm the calculations here developed, the source of disagreement may be then looked for in the neglect of BRIDGMAN's latent heat.

The mathematical difficulty of the problem consists in the existence of two distinct states determined by the magnetic field. The purpose of this paper is to point out some special solutions (particular integrals) of the problem.

We shall employ the electromagnetic system of units. By H (a vector) and by σ we shall denote the magnetic field and the resistivity. The symbol H_c will be used for the threshold value of the field. The resistivity σ may have either of two values σ_1, σ_2 , according as to whether $|H| > H_c$ or $|H| < H_c$. The value σ_2 is the microresidual resistivity and in a special case may be taken to be zero. The electric intensity at any point we shall denote by the

¹⁾ H. KAMERLINGH ONNES, Proc. Amst. Acad. Sc. 16, (2) 1914. Leiden Comm. N^o. 133, 139.

²⁾ F. B. SILSBEE, Journal Washington Academy 6, 597—602, 1916. Bureau of Standards Scientific Paper N^o. 307 (July 23, 1917).

³⁾ Journal Washington Acad. Vol. 11, p. 455, 1921.

vector E . The current density is then $\frac{E}{\sigma}$. If t be the time, the fundamental equations of the problem are:

$$\operatorname{div} H = 0 \quad \operatorname{curl} H = \frac{4\pi}{\sigma} E \quad (1)$$

$$\operatorname{div} E = 0 \quad \operatorname{curl} E = -\frac{\partial H}{\partial t} \quad (2)$$

Hence

$$\left(\nabla^2 - \beta \frac{\partial}{\partial t}\right) H = 0, \quad \beta = \frac{4\pi}{\sigma} \quad (3)$$

and in the case of cylindrical symmetry, H being parallel to the axis, the distance from which is r

$$\left(\frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} - \beta \frac{\partial}{\partial t}\right) H = 0 \quad (3I)$$

If only small penetrations from the surface are investigated the approximate form

$$\frac{\partial^2 H}{\partial r^2} = B \frac{\partial H}{\partial t} \quad (3II)$$

may be used. The equations (3), (3I), (3II) are analogous to equations in heat conduction and it is therefore of interest to follow out this analogy somewhat closer. In the case of cylindrical symmetry and

H parallel to the axis the electric intensity is by symmetry directed along a system of coaxial circles having the axis of symmetry for their common axis as shown on the figure (Fig. 1). Dropping now the meaning of E and H as vectors and denoting forthwith by E and H the absolute magnitudes of the electric and magnetic intensities, we have from (1) and (2)

$$-\frac{\partial H}{\partial r} = \beta E \quad (5)$$

$$\frac{1}{r} \frac{\partial}{\partial r} (rE) = -\frac{\partial H}{\partial t} \quad (6)$$

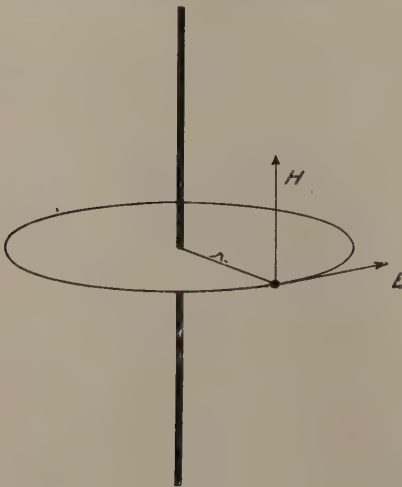


FIG. 1.

mathematically to STEFAN's problem of the propagation of the frost ¹⁾ though for one case a slight extension of his mathematical method will be necessary.

Case I. The material is supraconducting to start with, the field inside and outside is homogeneous and equal to $\overline{H}_1 < H_c$. Suddenly the field outside is increased to a value $\overline{H}_2 > H_c$.

We begin counting time from the instant of the sudden change. After the lapse of a time t the non-supraconductive state will have advanced a certain distance x_c into the metal. A moving plane separates the regions having the two values of σ . The low value σ_2 is on the right of this bounding plane while the high value σ_1 is on the left. Corresponding to the two values of σ here are two values of β on the right and left (β_2, β_1 respectively). On both sides of the surface of separation $H = H_c$. Also E must be continuous at the boundary. Letting

$$\Theta(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-u^2} du$$

we know from the work of STEFAN that it is possible to satisfy all the conditions of the problem by letting H on the left and on the right of the boundary have respectively the expressions:

$$H_1 = A_1 + B_1 \Theta\left(\frac{x}{2} \sqrt{\frac{\beta_1}{t}}\right) \dots \dots \dots (9)$$

$$H_2 = A_2 + B_2 \Theta\left(\frac{x}{2} \sqrt{\frac{\beta_2}{t}}\right) \dots \dots \dots (10)$$

In fact these satisfy (3^{II}) and by a proper choice of the constants A_1, B_1, A_2, B_2 the initial and boundary conditions can also be satisfied. The equations are

$$\begin{aligned} \overline{H}_1 &= A_1 & \overline{H}_2 &= A_2 + B_2 \\ H_c &= A_1 + B_1 \Theta\left(\frac{x_c}{2} \sqrt{\frac{\beta_1}{t}}\right) = A_2 + B_2 \Theta\left(\frac{x_c}{2} \sqrt{\frac{\beta_2}{t}}\right) \\ \frac{1}{\beta_1} \left(\frac{\partial H_1}{\partial x}\right)_{x=x_c} &= \frac{1}{\beta_2} \left(\frac{\partial H_2}{\partial x}\right)_{x=x_c} \end{aligned}$$

¹⁾ WEBER RIEMANN, Differentialgleichungen der Mathematischen Physik, VIEWEG und SOHN, 1919. Vol. II, pp. 117-121.

J. STEFAN, Wiener Monatshefte für Mathematik and Physik, I. Jahrgang, p. 1, 1890.

Sitzungsberichte der Wiener Akademie. Vol. 98, Div. IIa, p. 473, 1890.

It follows from the third of these that $\frac{x_c}{\sqrt{t}} = \alpha$ where α is constant.

On account of the constancy of α the fourth equation can also be satisfied. Eliminating the constants A, B we find for α :

$$\frac{\bar{H}_2 - H_c}{H_c - \bar{H}_1} = \frac{\sqrt{\frac{\beta_1}{\beta_2}} e^{\frac{\alpha^2 \beta_1}{4}} \Theta\left(\frac{\alpha}{2} \sqrt{\beta_1}\right)}{e^{\frac{\alpha^2 \beta_2}{4}} \left[1 - \Theta\left(\frac{\alpha}{2} \sqrt{\beta_2}\right)\right]} \quad \dots \quad (11)$$

The expression

$$\frac{e^{\frac{\alpha^2 \beta_1}{4}} \Theta\left(\frac{\alpha}{2} \sqrt{\beta_1}\right)}{e^{\frac{\alpha^2 \beta_2}{4}} \left[1 - \Theta\left(\frac{\alpha}{2} \sqrt{\beta_2}\right)\right]}$$

increases from 0 to ∞ as α increases from 0 to ∞ . We can deduce from this that whatever the values of $\bar{H}_1, \bar{H}_2, H_c$ may be (provided H_c is between \bar{H}_1 and \bar{H}_2) there is always one and only one value of α which satisfies (11). An increase in $|\bar{H}_2 - H_c|$ leads to an increase in α . An increase in $|H_c - \bar{H}_1|$ gives a decrease in α . Since β_1 is very large we are concerned with

$$\lim_{\beta_1 \rightarrow \infty} \sqrt{\beta_2} e^{\frac{\alpha^2 \beta_2}{4}} \left[1 - \Theta\left(\frac{\alpha}{2} \sqrt{\beta_2}\right)\right] = \frac{2}{\sqrt{\pi} \alpha}$$

whence by (11)

$$\sqrt{\pi} \frac{H_c - \bar{H}_1}{\bar{H}_2 - H_c} = \frac{e^{-\frac{\alpha^2 \beta_1}{4}}}{\frac{\alpha \sqrt{\beta_1}}{2} \Theta\left(\frac{\alpha \sqrt{\beta_1}}{2}\right)} \quad \dots \quad (12)$$

If $\bar{H}_1 = 0$ and if $\frac{\bar{H}_2 - H_c}{H_c}$ is $\sqrt{\pi}$ i. e. if the externally applied field is $2.77 H_c$ both sides of (12) are unity and hence $\frac{\alpha \sqrt{\beta_1}}{2}$ is the value of x that makes $x e^{x^2} \Theta(x) = 1$.

This value is about 0.77. Since β_1 is roughly 1 for tin the constant α is of the order of magnitude of 1.6 and the law of penetration of the boundary is $x_c = 1.6 \sqrt{t}$.

It may be shown that the field is unchanged in the bulk of the supra-conductor and that only a surface current is induced. From

this point of view the problem could be solved without reference to medium (2) by introducing a boundary condition in the medium (1) which is to express the fact that the flow $-\frac{1}{\beta_1}\left(\frac{\partial H}{\partial x}\right)_{x=x_c}$ is spent in supplying the quantity H to new regions of the material having initially $H=\bar{H}_1$ and converted to $H=H_c$. The length of the region converted per second is $\frac{dx_c}{dt}$ and thus the boundary condition is:

$$\left(\frac{\partial H}{\partial x}\right)_{x=x_c} + \beta_1 (H_c - \bar{H}_1) \frac{dx_c}{dt} = 0.$$

The problem can be also solved from this point of view.

This direct solution for the case $\beta_2 = \infty$ naturally leads to the same result which we have obtained by passing to the limit of $\beta_2 \rightarrow \infty$. It may be, however, that other problems may be more easily solved for the case of $\beta_2 = \infty$ by this method than by passing to the limit.

Case II. Penetration of supraconductivity into a non-supraconductor.

We next pass to the case of a material in which the supraconductivity has been destroyed by a magnetic field, we diminish the field from the outside so as to reestablish supraconductivity. The supraconductivity is reestablished first in the external layer of the metal and propagates inward as time goes on.

Fixing our attention again on Fig. 2 we suppose that just before $t=0$ the magnetic field H has a uniform value \bar{H}_1 throughout $x > 0$ and $x < 0$. This value \bar{H}_1 is greater than the critical field H_c . At $t=0$ the value of H at the left of AB is dropped to $\bar{H}_2 < H_c$.

After the lapse of a time t the boundary between the two conducting states will have advanced a distance x_c . For $x < x_c$ the metal is microresidually conducting and $\beta = \beta_1$. For $x > x_c$ the metal has its ordinary conductivity and $\beta = \beta_2$. The expression for H for $x < x_c$ will be written as H_1 . As in the first case we are induced to try to satisfy our equations by expressions of the form:

$$H_1 = A_1 + B_1 \Theta \left(\frac{x}{2} \sqrt{\frac{\beta_1}{t}} \right)$$

$$H_2 = A_2 + B_2 \Theta \left(\frac{x}{2} \sqrt{\frac{\beta_2}{t}} \right)$$

The initial and boundary conditions are:

$$\begin{aligned}\bar{H}_1 &= A_1 + B_1 & \bar{H}_2 &= A_2 \\ H_c &= A_1 + B_1 \Theta\left(\frac{x_c}{2} \sqrt{\frac{\beta_1}{t}}\right) = A_2 + B_2 \Theta\left(\frac{x_c}{2} \sqrt{\frac{\beta_2}{t}}\right) \\ \frac{1}{\beta_1} \left(\frac{\partial H_1}{\partial x}\right)_{x=x_c} &= \frac{1}{\beta_2} \left(\frac{\partial H_2}{\partial x}\right)_{x=x_c}\end{aligned}$$

The third of the four above written lines shows that $\frac{x_c}{\sqrt{t}} = \alpha$ where α is constant. Eliminating the constants A, B from the above equations the result for α is:

$$\frac{\bar{H}_1 - H_c}{H_c - \bar{H}_2} = \frac{\sqrt{\beta_1} e^{\frac{\alpha^2 \beta_1}{4}} \left[1 - \Theta\left(\frac{\alpha \sqrt{\beta_1}}{2}\right) \right]}{\sqrt{\beta_2} e^{\frac{\alpha^2 \beta_2}{4}} \Theta\left(\frac{\alpha \sqrt{\beta_2}}{2}\right)} \quad \dots \quad (13)$$

We are particularly interested in the meaning of this equation for the case of a very large β_2 . The values of α which satisfy (13) for this case must be very small because neither finite nor infinitely large values of α satisfy (13) in the case of an infinite β_2 . If α is very small the numerator of the right hand member of (13) reduces to $\sqrt{\beta_1}$. Therefore α must vanish at least as $\frac{1}{\sqrt{\beta_2}}$ for otherwise the

factor $e^{\frac{\alpha^2 \beta_2}{4}} \Theta\left(\frac{\alpha \sqrt{\beta_2}}{2}\right)$ will yield an infinite result. The presence of $\sqrt{\beta_2}$ in the denominator of (13) assures us moreover that α vanishes to a still higher order than $\frac{1}{\sqrt{\beta_2}}$. Therefore $\alpha \sqrt{\beta_2}$ is infinitesimal and

$$\Theta\left(\frac{\alpha \sqrt{\beta_2}}{2}\right) \approx \frac{\alpha \sqrt{\beta_2}}{\sqrt{\pi}}.$$

Hence (13) leads to:

$$\alpha = \sqrt{\pi} \frac{H_c - \bar{H}_2}{\bar{H}_1 - H_c} \frac{\sqrt{\beta_1}}{\beta_2} \quad \dots \quad (14)$$

if β_2 is very large. Thus the propagation of the boundary between the two states is infinitely slow if the microresidual resistance is infinitesimal. It should take an infinite time for the conductor to become entirely supra-conducting under the conditions just considered.

This result is of course a quite natural one from a purely non-mathematical point of view. The shielding power of the micro-residually conducting layer at AB (Fig. 2) is extremely great on account of its high conductivity. Thus in a finite thickness it transmits practically no magnetic field and as long as the magnetic field is transmitted the thickness of the microresidually conducting layer must be very small.

It is of interest to point out that even though the thickness of the microresidually conducting layer is very small the resistance of a square centimeter of this layer is finite and in the limit independent of σ_2 . In fact this resistance is:

$$\frac{\sigma_2}{\alpha \sqrt{t}} = 4 \sqrt{\frac{\pi}{\beta_1 t} \frac{\bar{H}_1 - H_c}{H_c - \bar{H}_2}} = 2 \sqrt{\frac{\alpha_1}{t} \frac{\bar{H}_1 - H_c}{H_c - \bar{H}_2}}$$

The formula (14) can be made clear also in the following manner. The microresidually conducting layer has two boundaries: one at $x=0$ and one at $x=x_c$. The value of H at the first is \bar{H}_2 and at the second it is H_c . The drop in H in the thickness x_c is $\bar{H}_2 - H_c$. Let us suppose that this drop takes place uniformly throughout the thickness x_c . Then the drop in H per unit length is $\frac{\bar{H}_2 - H_c}{x_c}$ throughout. This quantity divided by β_2 is by (7) the electric intensity E which must be continuous at the passage through $x=x_c$. To the right of $x=x_c$ the conditions for H are determined by the facts that $H=H_c$ for $x=x_c$ and $H=\bar{H}_1$ for $x=\infty$. Since x_c is practically zero we commit no sensible error by replacing the first of these conditions by $H=H_c$ for $x=0$. For this case it is clear that:

$$H = H_c + (\bar{H}_1 - H_c) \Theta \left(\frac{x}{2} \sqrt{\frac{\beta_1}{t}} \right)$$

and

$$-\frac{1}{\beta_1} \left(\frac{\partial H}{\partial x} \right)_{x=x_c} = \frac{1}{2 \sqrt{\beta_1 t}} \frac{2}{\sqrt{\pi}} (-\bar{H}_1 + H_c).$$

Since this is the same as $\frac{\bar{H}_2 - H_c}{\beta_2 x_c}$ the equation (14) follows. Thus the assumption of uniform drop of H in the microresidually conducting layer leads to a correct result.

Since x_c is very small it appears legitimate to generalize this conclusion and to assume generally that H drops off uniformly throughout the microresidually conducting layer even in the general

cylindrical case because the curvature of the surface can have no influence in the thickness x_c . Thus if the solution analogous to

$$H = H_c + (\overline{H}_1 - H_c) \Theta \left(\frac{x}{2} \sqrt{\frac{\beta_1}{t}} \right)$$

can be written down for the cylinder in question the solution for x_c offers no difficulty.

As an example let us consider a thin sheet of metal to which the magnetic field is applied from both sides tangentially to the surface. Let the thickness of the sheet be c . The solution given in WEBER RIEMANN (l.c.) Vol. 2, p. 112 formula II applies here. The constant a^2 is in our notation $\frac{1}{\beta}$. Thus according to this formula if H is suddenly changed by an amount $H_c - H_1$ on both sides of the sheet the change in the value of H at a point having a distance x from one of the sides and considered at the time t is:

$$(H_c - \overline{H}_1) \left\{ \frac{x}{c} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(-)^n}{n} e^{-\frac{1}{\beta_1} \left(\frac{n\pi}{c} \right)^2 t} \sin \frac{n\pi x}{c} + \right. \\ \left. + \frac{c-x}{c} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{(-)^n}{n} e^{-\frac{1}{\beta_1} \left(\frac{n\pi}{c} \right)^2 t} \sin \frac{n\pi (c-x)}{c} \right\}$$

This expression must now be differentiated with respect to x the value of the derivative with reversed sign at $x=0$ must be divided by β_1 and equated to $\frac{\overline{H}_1 - H_c}{\beta_1 x_c}$. This leads to

$$\beta_1 x_c = \frac{(\overline{H}_1 - H_c) c \beta_1}{2(H_c - \overline{H}_1) \vartheta_1 \left(0, e^{-\frac{4\pi^2 t}{\beta_1 c^2}} \right)} \quad (15)$$

where

$$\vartheta_1(0, q) = 2 \left[q^{\frac{1}{4}} + q^{\frac{9}{4}} + \dots \right].$$

It may be shown that (15) degenerates into (14) if $c \rightarrow \infty$.

The essential difference between (15) and (14) is that according to (15) for sufficiently high values of t the quantity $\beta_1 x_c$ is of the order of $e^{\frac{\pi^2 t}{\beta_1 c^2}}$ while according to (14) $\beta_1 x_c$ is always of the order \sqrt{t} . The increase in conductivity after a sufficient lapse of time becomes therefore very much more rapid than (14) would suggest.

The agreement between (14) and (15) is good as long as $\frac{4\pi^2 t}{\beta_1 c^2}$ is small because this assures the approximation of $\vartheta_2(0, q)$ by a probability integral. If $\beta_1 \leq 1$ and $c \leq 0.01$ cm. the quantity $\frac{4\pi^2 t}{\beta_1 c^2} \leq 3.9 \times 10^6 t$. The series for $\vartheta_2(0, q)$ is then approximately $2[e^{-10^6 t} + (e^{-10^6 t} q + \dots)]$. Thus t must be considerably less than 10^{-6} sec. if (14) is to be a good approximation.

If now we should deal with a magnetic field which is periodically applied and removed from the cylinder the above calculation must enable one to form an idea as to the average electrical resistance of the cylinder used with a current passing longitudinally. In fact the method of calculation which we used last applies not only in the case of a uniform initial state but also if this state is variable. The solution of any specific case would be connected of course with further calculations.

Case III. Sudden "reversal" of field.

Fixing our attention again on Fig. 2 let us suppose that just before $t=0$ the field has the uniform value $\overline{H}_1 > H_c$. At $t=0$ the field at $x=0$ is suddenly changed to $-\overline{H}_2$ where $\overline{H}_2 > H_c$.

After the lapse of a time t we may expect to find three regions in the metal. These will be separated by two critical values of x , say x_{c_1}, x_{c_2} , ($x_{c_1} x_{c_2}$). In the intervals $(0, x_{c_1})$, (x_{c_1}, x_{c_2}) , (x_{c_2}, ∞) β has the values $\beta_1, \beta_2, \beta_3$ respectively.

We shall try to satisfy the conditions of the problem by letting the magnetic field in these three intervals have the following expressions:

$$\begin{aligned} H = H_1 &= A_1 + B_1 \Theta\left(\frac{x}{2} \sqrt{\frac{\beta_1}{t}}\right) & 0 < x < x_{c_1} \\ H = H_2 &= A_2 + B_2 \Theta\left(\frac{x}{2} \sqrt{\frac{\beta_2}{t}}\right) & x_{c_1} < x < x_{c_2} \\ H = H_3 &= A_3 + B_3 \Theta\left(\frac{x}{2} \sqrt{\frac{\beta_3}{t}}\right) & x_{c_2} < x < \infty \end{aligned}$$

The equality between H_1 and H_2 at x_{c_1} and the equality between H_2 and H_3 at x_{c_2} leads to the conclusion that

$$x_{c_1} = \alpha_1 \sqrt{t}, \quad x_{c_2} = \alpha_2 \sqrt{t}$$

where α_1, α_2 are constants. Thus the boundary and initial conditions become:

$$-H_c = A_1 + B_1 \Theta\left(\frac{\alpha_1 \sqrt{\beta_1}}{2}\right) = A_2 + B_2 \Theta\left(\frac{\alpha_1 \sqrt{\beta_2}}{2}\right)$$

$$+H_c = A_2 + B_2 \Theta\left(\frac{\alpha_2 \sqrt{\beta_2}}{2}\right) = A_1 + B_1 \Theta\left(\frac{\alpha_2 \sqrt{\beta_1}}{2}\right)$$

$$\frac{B_1}{\sqrt{\beta_1}} e^{-\frac{\alpha_1^2 \beta_1}{4}} = \frac{B_2}{\sqrt{\beta_2}} e^{-\frac{\alpha_1^2 \beta_2}{4}}$$

$$\frac{B_2}{\sqrt{\beta_2}} e^{-\frac{\alpha_2^2 \beta_2}{4}} = \frac{B_1}{\sqrt{\beta_1}} e^{-\frac{\alpha_2^2 \beta_1}{4}}$$

$$\bar{H}_1 = A_2 + B_2 \quad ; \quad -\bar{H}_2 = A_1$$

Eliminating the constants A, B two equations in α_1, α_2 are obtained. These may be written in the form:

$$\begin{aligned} \frac{\bar{H}_2 - H_c}{e^{1/4 (\alpha_1^2 \beta_1 + \alpha_2^2 \beta_2)} \Theta\left(\frac{\alpha_1 \sqrt{\beta_1}}{2}\right)} &= \frac{\bar{H}_1 - H_c}{e^{1/4 (\alpha_1^2 \beta_1 + \alpha_2^2 \beta_2)} \left[1 - \Theta\left(\frac{\alpha_2 \sqrt{\beta_1}}{2}\right)\right]} = \\ &= \frac{2 H_c}{\sqrt{\frac{\beta_2}{\beta_1}} e^{1/4 (\alpha_1^2 + \alpha_2^2) \beta_2} \left[\Theta\left(\frac{\alpha_2 \sqrt{\beta_2}}{2}\right) - \Theta\left(\frac{\alpha_1 \sqrt{\beta_2}}{2}\right)\right]}. \end{aligned}$$

Since β_2 is very large the comparison of the first two expressions with each other shows that $(\alpha_2^2 - \alpha_1^2) \beta_2$ must remain finite. Thus writing

$$\beta_2 (\alpha_2 - \alpha_1) = \gamma \quad , \quad (\alpha_1 + \alpha_2) = 2\alpha \quad . \quad . \quad . \quad (16)$$

and considering only the case of very large values of β_2 we have

$$\left. \begin{aligned} \frac{\bar{H}_2 - H_c}{e^{\frac{\alpha_1}{2} + \frac{\alpha_2^2 \beta_1}{4}} \Theta\left(\frac{\alpha \sqrt{\beta_1}}{2}\right)} &= \frac{\bar{H}_1 - H_c}{e^{\frac{\alpha_2^2 \beta_1}{4}} \left[1 - \Theta\left(\frac{\alpha \sqrt{\beta_1}}{2}\right)\right]} = \\ &= \frac{2 H_c}{\lim_{\beta_2 \rightarrow \infty} \sqrt{\frac{\beta_2}{\beta_1}} e^{\frac{\alpha_2^2 \beta_2}{4}} \left[\Theta\left(\frac{\alpha_2 \sqrt{\beta_2}}{2}\right) - \Theta\left(\frac{\alpha_1 \sqrt{\beta_2}}{2}\right)\right]} \end{aligned} \right\} (16')$$

The limit last written is taken under the conditions (16), the quantities α, γ being kept constant. It is easily found that the *Lim*

in question is $\frac{2}{\sqrt{\pi \beta_1}} \frac{e^{\frac{\alpha \gamma}{2}} - 1}{\alpha}$.

Eliminating γ and letting

$$a = \frac{\alpha \sqrt{\beta_1}}{2}, \quad \tau = \frac{\overline{H}_1 - H_c}{H_2 - H_c} \quad \dots \quad (17)$$

the resultant equation for a becomes

$$\frac{2 H_c}{H_2 - H_c} = \frac{1}{\sqrt{\pi}} \frac{1 - (\tau + 1) \Theta(a)}{\Theta(a) [1 - \Theta(a)] a e^{a^2}} \quad \dots \quad (18)$$

Solving (16') for γ we obtain

$$\gamma = \frac{2}{\alpha} \log \frac{1 - \Theta}{\tau \Theta} \quad \dots \quad (19)$$

If $\tau = 0$ (18) becomes $\frac{2 H_c}{H_2 - H_c} = \frac{1}{\sqrt{\pi} a e^{a^2} \Theta(a)}$. This formula is readily seen to be in agreement with (12) if in the latter $\overline{H}_1 = -H_c$.

Thickness of Supra-Conductive Layers.

Formulas (14) (19) enable us to make an estimate of the thickness of supraconductive layers produced by the suppression or reversal of a strong magnetic field. Thus according to (14) the quantity a is of the order of $\frac{1}{\beta_1}$. Since β_1 is approximately 1, the thickness of the layer reached in 1 sec. measured in centimeters is of the order of magnitude of the ratio of the conductivities just above and just below the transition point. This ratio may be 10^{-8} and thus if formula (14) applies supra-conductive layers the thickness of which is of molecular dimensions are dealt with.

If the thickness of the slab discussed in (15) is 1 cm., the first term of the series $\mathcal{O}_2 \left(0, e^{-\frac{4\pi^2 t}{\beta_1 c^2}} \right)$ is $2 e^{-4\pi^2 t}$ (β_1 being set = 1). Thus if $t = 10^{-4}$ sec. (14) and (15) are nearly in agreement and the effect of finite dimensions is not sufficient to throw off the conclusion just drawn because 10^{-4} sec. is a comparatively easily measurable interval of time.

The thickness of the supra-conductive layer brought about by the reversal of the field is according to (19) and (16)

$$\frac{\gamma \sqrt{t}}{\beta_2} = \frac{2 \sqrt{t}}{\alpha \sqrt{\beta_2}} \log \frac{1 - \Theta}{\tau \Theta}$$

and is thus of the same order of magnitude.

It is also of interest to observe that the amount of heat dissipated by the eddy currents in the microresidually conducting layer is

finite. In fact we have shown that the resistance of the layer per cm^2 is finite and further the current sheet in the layer has a finite strength being $\frac{1}{4\pi}$ of the difference in H on the two sides. Thus for the Case II the amount of energy dissipated per cm^2 is

$$\frac{1}{8\pi} \sqrt{\frac{\sigma_1}{t}} (\bar{H}_1 - H_c) (H_c - \bar{H}_2)$$

The sudden change in temperature which would have to be produced at the surface in order to supply this amount of heat would be given by

$$\Delta\theta = \frac{\sqrt{\pi}}{8} \sqrt{\frac{\sigma_1}{CK}} \frac{(\bar{H}_1 - H_c) (H_c - \bar{H}_2)}{4.19 \times 10^7}$$

and is insignificant.

Other considerations for periodic alternating fields indicate that heating may be an important factor, the danger being in eddy currents in the part of the conductor having $\sigma = \sigma_1$.

S U M M A R Y.

Special cases of the propagation of changes in magnetic field in a supra-conductive metal are discussed. The calculations show that with the assumptions made (treatment of the conductor as a continuous medium) the thickness of the supra-conductive layers involved may be of the order of molecular dimensions during perceptible intervals of time.

The writer wishes to express his gratitude to Professor LORENTZ for his criticism and advice.

Biochemistry. — *“Further Researches on the Antagonism between Citrate and Calcium Salt in Biochemical Processes, Examined by the Aid of Substituted Citrates”*. (First Communication).
By Dr. J. R. KATZ. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated at the meeting of May 26, 1923).

1. *Exposition of the Problem.*

In an earlier research¹⁾ I have tried to analyse the nature of the biological citrate action. After addition of citrate a biological liquid behaves as if it no longer contains any free calcium ions; addition of citrate acts, therefore, in the same way as addition of oxalate or fluoride. With this difference, however, that the action of the latter salts rests on the formation of a very little soluble precipitate, and that a gypsum solution remains perfectly clear after addition of citrate. Complex ions must, therefore, have been formed²⁾; it is only the question, how they are constituted.

In order to bring light in this still dark question, I compared at the time the action of the citrates with that of substituted citrates, in which one or more of the groups which possibly can bind the Ca to complexes (the alcohol group and the three carboxyl groups) were made inactive by substitutions (acetylation of the alcohol group; the carboxyl group esterified or converted to acid amide etc.). As typical representative of a biological citrate action the inhibition of the rennet coagulation of milk was investigated.

It then appeared that when either the alcohol group or one of the carboxyl groups is made inactive, the citrate action in a $\frac{1}{100}$ N. solution is reduced to $\frac{1}{10}$ of its strength; (i. e. is made equally weak as in a citrate solution of $\frac{1}{10}$ of the same strength), the removal of two or more groups reducing the action to less than $\frac{1}{100}$ of the original value. When the alcohol group is made inactive, the action appears to be equally strong as in other tri- or tetra-basic acids of allied structure, but without oxy-group (as tri-carballylic acid, aconitic acid or iso-allylene tetra-carbonic acid. When one

¹⁾ These Proc. Vol. XV, p. 434.

²⁾ SABATANI, Atti della R. Acad. di Torino 36, p. 27—53 and Memorie (2) 52, p. 213—257 was the first to adduce arguments for this theory.

BROMBERG, Diss. Amsterdam.

carboxyl group is made inactive, the action appears to be equally strong as in other bi-basic oxy-acids (as apple acid and tartaric acid). In the same way it appears that when two or three groups are made inactive at the same time, the action has become as great as in the then comparable compounds.

Now the question rises.

1. *is it also possible to prove such a diminution of the number of free Ca-ions in less complicated systems than such biochemical ones by the addition of citrate?*

2. *do the substituted citrates show there a similar diminution of activity as in rennet coagulation?*

The best way to answer these questions — the determination of the concentration of the free Ca-ions in the original solutions — is unfortunately barred, because we do not know a method as yet to determine the concentration of free Ca-ions potentiometrically. It is, therefore, necessary to have recourse to indirect methods. The most natural proceeding is to determine how much calcium is held in solution by addition of citrate, when a substance that precipitates the calcium as insoluble compound (e.g. oxalate, fluoride, pyrophosphate, soap etc.) is added to a diluted solution of a calcium salt. The solubility product of this reaction must be chosen so that the action of the citrate manifests itself so as to be easily measured. If this solubility product is known, the percentage of *free* calcium ions is known at least at this small concentration, while it is known how much Ca remains in solution. ¹⁾

The purest results will be obtained by an analytical determination by weight of the quantity of the calcium that has been precipitated or that has remained in the solution, as this can be carried out without appreciably diluting the calcium solution. I shall perform this experiment later on with citrate and with substituted citrates. But in order to get a preliminary rough idea, a titration can also be used, though this has the objection of appreciably diluting the original solution.

Mr. D. P. ROSS VAN LENNEP, who assisted me in my experiments on the influence of substituted citrates on rennet coagulation, pointed out to me that the soap-titration of calcium after CLARK (as it is used in the determination of the hardness of water) might render us good services here. ²⁾ He carried out a number of experiments

¹⁾ The question in how far hydrolytic decomposition complicates the matter, will be treated later.

²⁾ A drawback of this method is that the titration does not take place with water, but with 56-volume percentage alcohol, which changes the surroundings

with citrates and substituted citrates, but our experiments were left unpublished. I have again occupied myself with this problem, and performed a number of new determinations as a supplement and check. The results follow.

2. *Experiments.*

The examined Ca-solution, which was strongly split up into ions, was prepared as follows. A saturated solution of CaSO_4 (puriss. pro avel.) in distilled water was diluted with the 2,3 fold volume of distilled water. In a narrow-mouthed glass jar of 250 cm³. capacity 50 cm³ of this liquid was pipetted off and mixed with 50 cm³ of distilled water or with cm³ of an aqueous solutions of the substance under consideration. These 100 cm³ were titrated in the same glass jar by CLARK's method (with a solution of soap in alcohol of 56 volume percentages.¹⁾ In the titration a finely divided precipitate of calcium moleate is formed in the bottle. The endpoint has been reached when by the side of this precipitate so much alkali-oleate remains in the solution that, after shaking, the solution exhibits a not disappearing soap froth. As endpoint was taken the condition at which after a from six to eight times repeated vigorous shaking in the longitudinal axis of the bottle, the soap froth appears at the rim of liquid and bottle, as a white ring, 1 mm. high and from 1 to 2 mm. broad, and remains thus for five minutes. This endpoint can be determined pretty sharply, when the necessary practice has been obtained; when comparing experiments are always carried out in the same way, repeated determinations of the same liquid with a quantity of titration liquid of about 45 cm.³ deviate only some tenths of cm.³ from the mean of the determinations. For our determinations this accuracy is amply sufficient.

Without citrate the 100 cm.³ of calcium sulphate solution require from 45 to 47 cm.³ of titration liquid to reach this end-point; hence the total volume of the liquid at the end of the titration amounts to 145 or 147 cm.³. If in consequence of the addition of citrate the liquid required considerably less titration liquid, I added so much alcohol of 56 volume percentages (spec. gr. 0,921) from a burette to the 100 cm.³ that was to be examined, that at the end of the titration the total volume would again be between 145 and

in which the calcium ions are dissolved. If, however, only small differences are measured, in other words if about an equal amount of alcohol is added, this does not prevent us from obtaining *comparable* results.

¹⁾ I refer for an accurate description of CLARK's method to *Jahresberichte f. Chemie* 1850, p. 608; to LUNGE and BERL, 6th edition. Vol. II, p. 232.

147 cm.³; and in this liquid the endpoint was determined. This precaution was omitted, when the total volume was between 140 and 147 cm.³ at the end of the experiment. This measure purposes to prevent that in an inquiry into the titratable calcium in salt solutions of the same molecular concentration, these would have different molecular concentration at the endpoint of the titration, and would no longer be comparable for this reason.

1/10 N neutral solutions of the sodium salts were made from citric acid and its various substitution products (neutral towards litmus; it was verified that they remained neutral towards litmus on dilution with the same volume of the above gypsum solution). As normal solutions were considered those that contained one gramme-molecule per litre (hence not: One gramme-equivalent in multi-basic salts). The mixture of gypsum and of (perhaps substituted) citrate accordingly contained the various salts in the concentration of 1/20 N.

The gypsum solution diluted with the same volume of water consumed on an average 45.7 cm.³. This corresponds with 12.2 parts of CaO per 100000 parts of water; or with 8.7 parts of Ca per 100000 parts of water. In citrates etc. it was derived from a table of LUNGE and BERL¹⁾ (calculated from experiments by FAIST and KNAUSS), how much Ca was *not* found back in the titration, calculated as percentage of the total quantity (8.7).

In the first column is given the consumed quantity of cm.³ of titration liquid; in the second column the quantity of calcium that was not found back as percentage of the total quantity.

Thus I found:

a. <i>Citric acid</i> ²⁾	2.6 cm ³	96 %.
b. <i>Te alcohol group made inactive.</i>		
<i>Acetylcitric acid</i>	40.9 cm ³	12 %.
Compared with:		
<i>Aconitic acid</i>	41.3 cm ³	11 %.
<i>Tricarballic acid</i>	40.8 cm ³	12 %.
<i>Isoallylene tetra carbonic acid</i>	39.8 cm ³	14 %.
c. <i>One carboxyl group made inactive.</i>		
<i>Symmetrical citric acid monoamide</i>	41.1 cm ³	11½ %.
Compared with:		
<i>Apple acid</i>	40.2 cm ³	13½ %.
<i>Tartaric acid</i>	40.4 cm ³	13 %.

¹⁾ 6th edition, Vol. II, p. 232.

²⁾ When so few cm.³ of titration liquid are sufficient to reach the limiting value, the limit is much less easy to determine than it is otherwise, and the observations differ much more from each other.

d. One alcohol group and one carboxyl group made inactive.

<i>Methylene citric acid</i>	43.4 cm ³	5½ %
Compared with:		
Ambric acid	43.6 cm ³	5 %
Glutaric acid	43.6 cm ³	5 %
Acetone dicarbonic acid	43.9 cm ³	6 %

e. Two carboxyl groups made inactive.

<i>Citric acid dimethyl ester</i>	43.35 cm ³	5½ %
<i>Citro diamide</i>	43.75 cm ³	5 %

f. Three groups made inactive.

<i>Citramide</i>	44.4 cm ³	3 %
<i>Di ethylester of citric acid monoamide</i>	44.8 cm ³	3 %

Various indifferent salts of monovalent acids (sodium chloride, cyanide, formiate, acetyl-salicylate etc.) consume 44.6 to 44.9 cm³ of titration liquid; hence also three per cent less than water.

I refer for the structure formulae of the examined compounds to my previous publication¹⁾, where I have indicated them all.

It appears from these experiments that substitution in the citrates very considerably diminishes the action. If one group is made inactive (it seems to be immaterial whether it is the alcohol group or one of the carboxyl groups), about 11 or 12 % of the calcium is not found back in the titration (instead of 96 %). This quantity is, therefore, bound in complexes in the Ca-ion concentration which corresponds to the solubility of calcium oleate in an alcohol-water-mixture of about 17 volume percentages of alcohol (per 100 volume percentages of liquid mixture). In these solutions the compared citrates and substituted citrates are present in the same molecular concentration.

When two active groups are removed at the same time, about 5 or 5½ % of the calcium appears to be bound in complexes, in three groups only 3 %.

To be able to ascertain to what concentrations of the not-substituted citrate these values correspond, I have carried out some determinations with citrate of much weaker molecular concentration (all this expressed in the same units as in the experiments described before).

1/200 N citrate	(0.0050 N)	35.9 cm ³	24 %
1/400 N citrate	(0.0025 N)	42.55 cm ³	7.7 %
1/800 N citrate	(0.00125 N)	44.3 cm ³	3.4 %
no citrate		45.7 cm ³	—

¹⁾ These Proceedings. Vol. XV, p. 434.

Through interpolation it is found that 11 or 12 % of not recovered calcium corresponds to 0.0033 N; 5 or 5½ % to 0.0019 N citrate, and 3 % to 0.0010 N citrate; hence that the activity is reduced resp. to $\frac{1}{16}$, $\frac{1}{20}$, $\frac{1}{60}$ of its value through the substitution in the unchanged citric acid.

These values show good agreement with the results of the rennet coagulation experiments, where $\frac{1}{16}$, $\frac{1}{100}$, $\frac{1}{100}$ was found. In view of the uncertainty in the determinations with small quantities of complex formation no better agreement can be desired.

We may still point out that also barium and strontium salts are deprived of their free ions by addition of citrate. Thus I found in diluted solutions of barium nitrate, strontium nitrate and calcium sulphate, which required resp

barium	strontium	calcium
23.0 cm ³	25.4 cm ³	25.4 cm ³

of titration liquid, that — when these 100 cm³ contained $\frac{1}{100}$ resp. $\frac{1}{60}$ N sodium citrate — they consumed only:

$\frac{1}{100}$ N	21.6 cm ³	6.0 cm ³	11.2 cm ³
$\frac{1}{60}$ N	16.85 cm ³	1.85 cm ³	3.9 cm ³

3. Conclusion.

a. The biological citrate action rests on the diminution of the concentration of the free calcium ions through formation of complex compounds or ions. This citrate action can also be shown in less complicated systems than biochemical ones, e.g. in the solubility of calcium oleate in citrate.

b. Substituted citrates show there exactly the same diminution of activity as has been observed in a biochemical reaction (as the rennet coagulation). When either the alcohol group, or one of the carboxyl groups is removed, the activity is reduced to $\frac{1}{16}$ of its value; this diminution is much greater when two groups are removed at the same time.

c. Citric acid owes its strong activity to the fact that it is a multi-basic oxy-acid.

Experiments with other multi-basic oxy-acids are in progress. I refer for the literature to the extensive German publication, which will shortly appear.

Colloidchemistry. — "*Researches on the Nature of the So-Called Adsorptive Power of Finely-Divided Carbon.*" I. *The Binding of Water by Animal Carbon.* By Dr. J. R. KATZ. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated at the meeting of June 30, 1923).

I. *Introduction.*

The power of finely divided carbon to bind all kinds of substances is evidently in connection with the degree of fineness of division; for in not finely divided condition the carbon does not show this property. At present the phenomenon is almost universally considered as a typical example of real surface adsorption, i.e. as the accumulation of a substance in the boundary layer simply in consequence of the surface-forces.

This surface adsorption is generally considered as in sharp contrast with the formation of a solid solution. In the latter case the bound substance is not only found in the boundary layer solid-liquid, but through diffusion it gradually penetrates between the molecules of the solid substance, so that finally the principal quantity of the absorbed substance is not found in the boundary layer, but homogeneously distributed throughout the solid body.

A clear realization of the questions that can be solved by experiments on the nature of this binding to carbon only dates from the time of physical chemistry. BANCROFT¹⁾ and others have considered the possibility that the substances would have been absorbed by the carbon in solid solution; but the further development of this thought failed on account of the form of the binding-isotherm. If we had to do with a solid solution, — this was the opinion some twenty years ago — the laws of HENRY and NERNST must be valid, hence the quantity of absorbed substance must be in direct ratio to the concentration of the vapour and liquid phase, with which it is in equilibrium. A curve is, however, obtained which is almost horizontal at first, and which then turns its convex side downward. This might be explained by the assumption that the absorbed substance dissociates in the carbon into many (e.g. four

¹⁾ The Phase Rule.

or ten) molecules. In most of the substances bound by carbon such a hypothesis has no sense. Besides it does not become clear why the carbon works the better as it is more finely divided; this must then be accounted for as a consequence of the easier diffusion.

In 1907 FREUNDLICH showed ¹⁾ that the binding isotherm can be represented by the formula:

$$\frac{x}{m} = \alpha \cdot c^{\frac{1}{n}}$$

for not too great values of c (m is the quantity of carbon, x the substance bound by it, c the concentration of this substance in the solution which is in equilibrium with the carbon, α and n are constants). He showed that we had to do here with *real* equilibria which are established within a very short time. The degree in which a solid substance binds, varies greatly with the absorbed substance, but is little dependent on the nature of the solid phase. FREUNDLICH demonstrated that these facts become perhaps most easily comprehensible when it is assumed that the binding rests on surface adsorption, on a becoming denser of the surface of the solid phase. But in 1909 he himself does not exclude the possibility that the phenomenon rests on the formation of a dissociable chemical bond or a solid solution: he only calls these explanations "wesentlich unvorteilhafter" ²⁾).

In course of time, however, in default of new arguments for the other conceptions, this view has gained so many adherers that it often makes the impression as if it were an established fact that the sorption by carbon rests on a real surface-adsorption.

In 1910 I succeeded ³⁾ in showing that a deviation from the laws of HENRY and NERNST in solid solutions can have another cause than the dissociation of the bound substance into molecules, viz. when the mixing in solid solution is *chiefly* caused by the *attraction* between the molecules of solvent and dissolved substance; whereas in the ordinary diluted solutions the mixing is brought about particularly by the *diffusion impulse* (because mixing is a more probable state, one that takes place with increase of entropy — also when the attraction may be neglected). In this case the decrease of free energy is about equal to the heat effect that takes place in the

¹⁾ Zeitschr. f. physik. Chemie **57**, p. 385 (1907).

²⁾ Kapillarchemie, 1ste Aufl. p. 289, Akadem. Verlagsgesellschaft Leipzig 1909.

³⁾ These Proc. Vol. XIII, p. 958: Address at the Meeting of the Bunsen-Gesellschaft. Kiel, 1911; Gesetze der Quellung, Kolloidchem. Beihefte Bd 9.

binding. If the differential binding heat is great, and if it decreases on absorption of the substance, then follows from the equality of the variations of free energy and of binding-heat that the binding isotherm must have a course as FREUNDLICH must have found, i. e. that it begins pretty well horizontally, and then turns its convex side downwards. This appears to be the case in aqueous solutions of sulphuric acid and phosphoric acid, and in the swelling albumens and polysaccharides. In all these cases FREUNDLICH's formula appears to hold as approximating formula for small concentrations, even particularly well in aqueous solutions of sulphuric acid and phosphoric acid, though we have certainly not to do here with real surface adsorption, but with real mixing.

Hence it is clear that the validity of FREUNDLICH's formula does not furnish the proof that we have to do with surface adsorption. Inversely the equality in the variation of free energy and heat-effect is no proof either that there exists an ideal concentrated solution. It does not seem improbable to me that this equality also exists with pure surface adsorption, and possibly with many complicated intermediary phenomena called sorption at present. I found it confirmed in the absorption of water by cupri ferro cyanide, in which a strong change of colour from violet black to light brown is found¹⁾. The next step is now in my opinion to test this relation by a number of typical examples of genuine surface adsorption and of sorption. For if it appears to be valid everywhere, this is an important contribution to the knowledge of the sorption phenomena; and if it holds in some cases and not in others, it may be studied on what this depends. But apart from this it leads to a better method of analysis of sorption and adsorption phenomena: the simultaneous determination of the sorption isotherms and of the sorption heats. This method gives a much deeper insight than the prevalent one, which is restricted to the determination of the sorption isotherm for small concentrations. That FREUNDLICH's formula is of such universal validity at these small concentrations, will probably appear to mean that (in a system in which the variations of free energy and of heat-effect are equal in approximation) the differential sorption heat is very great at first, and diminishes gradually during the absorption; the longer the (almost) asymptotic horizontal initial part of the isotherm, the longer the differential sorption heat will preserve a great value. What is important in this method of investigation of the sorption phenomena is further that

¹⁾ Verslag van de gewone vergadering der wis- en natuurk. Afd. Kon. Akad. v. Wet. Dl. XXXI, Nos. 9-10, p. 542.

it can take into account not only the course of the isotherm for small concentrations, but the whole course. And besides it has the advantage that it does not bind itself beforehand by a preconceived opinion on the question which can at present mostly not be decided, of what nature the sorption phenomenon is (solid solution real surface adsorption, dissociable chemical combination, or two or three of these possibilities at the same time). The simultaneous determination of the two curves does, however, supply a collection of facts important for the decision of this question, which every theory has to take into account.

2. *Experiments.*

The purest animal carbon of MERCK was used for the investigation. It was placed in air-dry condition in a wide-mouthed glass jar; its water content was determined at 230° C. after 3 hours' drying. It is not impossible that in this way the water percentage is found slightly too high, the weight of the carbon having possibly been slightly diminished by oxidation. As in most hygroscopic substances of this kind it remains somewhat arbitrary *what* is considered to be "dry" substance.

For the determination of the *sorption heats* quantities of from 5 to 12 grammes of carbon were weighed in *air-dry* condition, which can easily be done accurately, as the substance is not particularly hygroscopic in this condition; the carbon cannot be weighed accurately when quite dry. In crystallisation dishes these samples of carbon were brought in exsiccators over sulphuric acid-water mixtures of different strengths; we then waited till equilibrium had been approximately established. In this way samples of carbon were obtained in which the water was very uniformly distributed. Where the water-content of the air-dry carbon was known, the increase or decrease of weight of the sample of carbon yields its water content at the known vapour tension.

This carbon was placed in a glass tube, which was closed with a tight-fitting rubber stopper and placed in a calorimeter vessel filled with water. The experiments were made in a room in which the temperature was particularly constant. After temperature equilibrium had been established, the course of the thermometer was followed; then the contents of the tube were emptied into the water of the calorimeter vessel, after which the temperature was again observed. After from 2—4 minutes the generation of heat did not increase appreciably any longer.

Let us call i the degree of sorption (gr. of water per 1 gr. of dry substance), and W the heat of sorption (generation of heat in cal. when 1 gr. of dry substance absorbs 1 gr. of water). Then I found:

i	Quantity of heat at maximum sorption per 1 gr. of dry carbon	W
0.—	20.91	0.—
0.049	17.66	3.25
0.090	15.34	5.57
0.218	11.79	9.12
0.350	7.90	13.01
0.437	6.05	14.86
0.563	3.12	17.79
0.659	1.59	19.32
0.718	1.09	19.82
0.753	0.29	20.62
sorption-max. 0.93	0.—	20.91

This is the integral heat of sorption. From this I calculate the differential heat of sorption for $i = 0$

$$\left(\frac{dW}{di}\right)_{i=0} = 75 \text{ cal.}$$

This value is considerably smaller than was found in swelling substances (250 to 400 cal.). At the heat of mixing of sulphuric acid (with water) it amounted to 550 cal., of phosphorus 100 cal., of glycerine 20 cal.

The curve of the integral sorption heats is graphed in fig. 1; it starts as the ordinary curve of the heats of imbibition and of mixing, as a hyperbola, then follows a flattened, almost rectilinearly rising part, the end again being a hyperbola. Accordingly it is distinctly different from the curves described by me formerly for bodies that can swell up.

I have not yet succeeded in calculating the differential sorption heat in its full course from these measurements. The curve of the integral sorption heat has so complicated a shape that a formula with a great number of parameters is required to give any description of it. The greater the number of parameters, the more arbitrary is

the calculation of the differential quotient $\frac{dW}{di}$. But this at least may

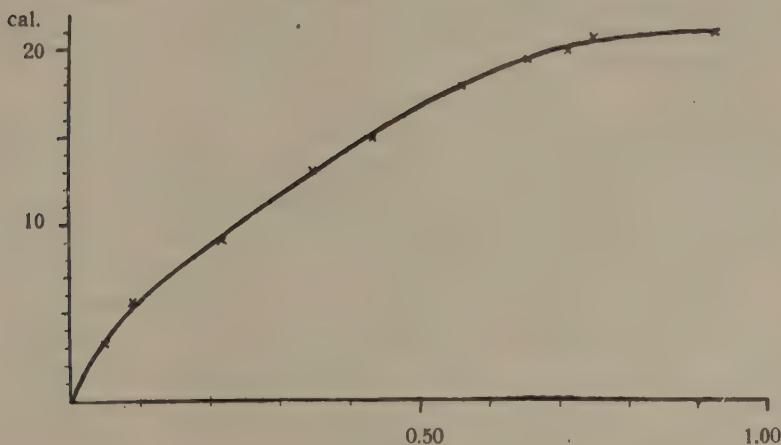


Fig. 1.

be said now that the curve begins with $\frac{dW}{di} = 75$ cal., then decreases pretty rapidly, in a way, which corresponds pretty closely with the course of this quantity in the heats of mixing (of sulphuric acid or phosphoric acid with water). At $i = 0.10$ to $i = 0.15$ it begins to assume a more or less constant (albeit slowly diminishing) value, amounting to about 23 cal., which diminishes again greatly past $i = 0.65$, and converges to zero.

It would be very important also to study the volume contraction at the absorption of water; for, where in expansible and in miscible substances the relation $\left(\frac{c}{W}\right)_{i=0}$ always appeared of the same order of magnitude (between 10 and 30×10^{-4}), it would be important to examine what the order of magnitude of this quotient would be in animal carbon. Unfortunately it is not possible to determine these volume contractions, as carbon probably acts as an adsorbent on every pycnometer liquid, at least in anhydrous condition.

The *free energy* at the sorption can most easily be calculated from the vapour tension of the water at different degrees of sorption. These vapour tensions have not been determined directly, but indirectly by the method of GAY LUSSAC-VAN BEMMELN (by bringing the substance into equilibrium with sulphuric acid-water mixtures of known strength till constancy of weight is reached). The absorption and loss of water then appeared to be a phenomenon of equilibrium, which presents *hysteresis*. This result is in striking

contrast with FREUNDLICH's experience that the absorption of *dissolved substances*, as iodine, dyestuffs, and organic acids, is an equilibrium, which is readily established independent of the condition from which one starts, and within a few minutes; this observation of FREUNDLICH's was confirmed for *dissolved* substances by many investigators.

In order to obviate the influence of hysteresis, the equilibrium had to be determined from two sides; then the approximative value of the state of equilibrium was calculated by taking the mean of the two values found in this way. Accordingly twice thirteen samples of air-dry carbon, each having a weight of about one gramme, were weighed off in crystallisation dishes. One half of these dishes were dried for one or two weeks in a vacuum exsiccator over sulphuric acid; they then contained no more than 1 or 2 parts of water to 100 parts by weight of dry carbon. The other half was placed over water in a vacuum exsiccator for the same length of time; they then contained about 90 parts of water to 100 parts of dry carbon. Then thirteen small exsiccators were arranged with sulphuric acid-water mixtures of known vapour tension; in every exsiccator there was placed a dry and a moistened carbon. These acids were refreshed a few times. After 40—90 days, when the dishes had become almost quite constant of weight long before, it was assumed that they had reached their onesided equilibrium. All the experiments took place at a temperature of 16—20° C. in a room in which the variations of temperature were particularly small (a room built specially for thermochemistry).

The vapour tension h was expressed as fraction of the maximum tension of water at the same temperature; the sorbed quantity i as grammes of water per one gramme of dry carbon. The free energy at the sorption of one gramme of liquid water is found from the relation $A = \frac{1252}{18} \log^{10} h$.

Fig. 2 shows the isotherm. The curve begins as a real adsorption-curve (or as the isotherm of a concentrated solution), but with a *very* short horizontal initial portion¹⁾, at half its height, ($h = 0,40$ to $0,65$) it gets, however, an almost horizontal part; at $h = 0,65$ and $i = 0,57$ there begins a new part of the curve (which, however, issues from the preceding part without any abrupt transition), which again has an S-shape. It is remarkable how great the quantity

¹⁾ This has probably been drawn too long; has the weight of the carbon not been somewhat diminished by drying at 200° C. through oxidation? The horizontal beginning, *if* it exists, is probably only little pronounced.

of water is which this form of amorphous carbon can absorb; over a sulphuric acid with a $h = 0.997$ the substance absorbed 0.929 parts of water per 1 part of dry substance! Accordingly an absorption of water of the same order of magnitude as in *greatly* swelling

h	i			Difference between the two false equilibria
	after moistening	after drying	in equilibrium	
0.010	0.009	0.022	0.016	—
0.083	0.033	0.021	0.027	—
0.176	0.039	0.038	0.039	—
0.278	0.062	0.052	0.057	0.010
0.410	0.172	0.141	0.157	0.031
0.517	0.458	0.266	0.362	0.192
0.596	0.570	0.411	0.491	0.159
0.721	0.649	0.572	0.631	0.077
0.788	0.673	0.631	0.652	0.021
0.853	0.698	0.676	0.687	0.022
0.914	0.730	0.715	0.723	0.015
0.962	0.800	0.814	0.807	—
0.997	—	0.929	0.929	—

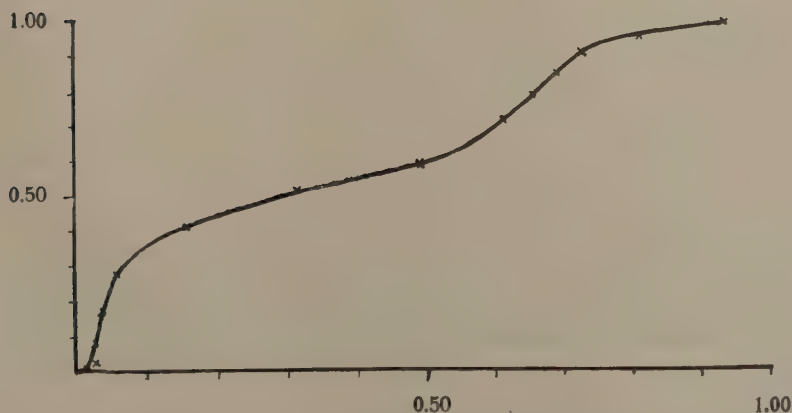


Fig. 2.

substances. BACHMANN¹⁾, who already determined an isotherm of carbon and water before me, found in cocoanut carbon a maximum water absorption of $i = 0,25$. BERL and ANDRESS²⁾ also found in their carbon a considerably smaller value than I in mine.

The double-S-shaped curve of the isotherm obtained is practically the same form as that which VAN BEMMELEN has observed in gels of silicic acid and of iron hydroxide. The flat portion there corresponds to the part of the curve in which the gel, which is first transparent, becomes opaque.

3. Comparison of Free Energy and Heat Effect.

A simple comparison of the curves fig. 1 and fig. 2 shows that $\frac{dW}{di}$ and $\log h$ must have an analogous course as function of i . Both curves have an almost horizontal, almost rectilinear (slowly descending) portion between $i = 0.10$ and $i = 0.60$ to 0.65 ; both curves have before and after this the shape as for liquids which mix with water with strong heat effect. By graphical determination of the differential quotient $\frac{dW}{di}$ this can be estimated for some values of i , for which $\log h$ is known. Thus I find:

i	h	$\frac{1252}{18} \log^{10} \frac{h_1}{h_2}$	$\left(\frac{dW}{di}\right)_1 - \left(\frac{dW}{di}\right)_2$
0.027	0.083	37 cal	11 cal
0.057	0.278	12 "	20 "
0.157	0.410	7 "	8 "
0.362	0.517	4 "	4 "
0.491	0.596	6 "	4 "
0.631	0.721	5 "	5 "
0.687	0.853	3.5 "	6 "
0.867	0.962		

These are only rough estimations; but they show nevertheless with sufficient probability that in the large middle portion of the curve (from $i = 0.05$ to $i = 0.80$) the variation of the free energy

¹⁾ Zeitschr. f. anorgan. Chemie 100, p 32 (1917).

²⁾ Zeitschr. f. angewandte Chemie 1921. Bd. I.

is of the same order of magnitude as the heat effect. But with small i the heat effect is much smaller than the variation of the free energy. This latter is probably in connection with the small value of the first differential heat of sorption in this substance. Most likely there is no equality in the middle piece either, but only correspondence in the order of magnitude. The experiments are, however, not accurate enough to set forth this difference clearly.

4. *The Analogy of the Curves with those for Newly-made Silicic Acid and ZSIGMONDY and ANDERSON's Explication.*

As I already observed, the isotherm has the same typical shape as that found by VAN BEMMELEN and later by ANDERSON for silicic acid gel. The "turn", the point where the second S-shaped curve begins, lies at $i = 0.57$ and $h = 0.65$ for carbon. Also BACHMANN found a curve with a horizontal portion for the cocoanut carbon examined by him (possibly even with two such pieces). And BERL and ANDRESS found a curve of the same shape as mine in the carbon examined by them.

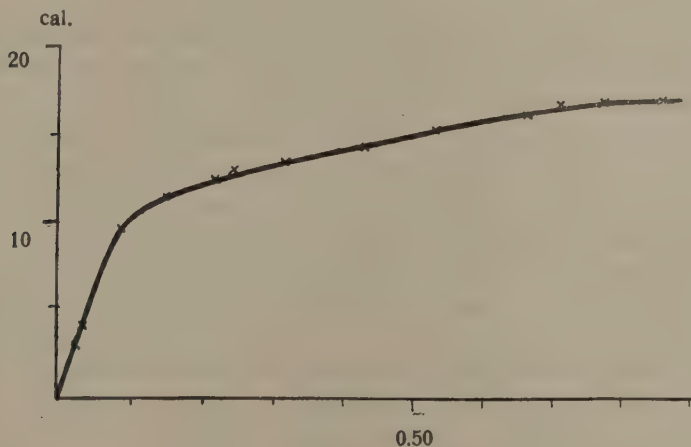


Fig. 3.

That also the curves of the heats of sorption correspond is shown by fig. 3, in which I have represented BELLATI and FINAZZI's results ¹⁾ for newly-made silicic acid (temperature 12°—20° C.). Unfortunately these carefully performed researches have so far escaped the notice of the writers of the books on colloid chemistry, whence they have not met with the recognition they deserve. The curve typically

¹⁾ M. BELLATI and L. FINAZZI, Atti d. R. Instituto Veneto, Serie VIII, Tomo 4, p. 518.

presents the same course as that found by me for carbon; the initial part as the curve for a heat of mixing, the almost rectilinear middle portion, the end in a curve with the concavity downward. Unfortunately we have no reason to believe that the silicic acid examined by BELLATI and FINAZZI possesses exactly the same constants as that on which VAN BEMMELEN and ANDERSON performed their determinations of the vapour tension, as the properties greatly depend on the preparation. This is, however, the case in the experiments with carbon, described above.

In the absorption of water vapour by carbon we have, therefore, to do with a system of which the isotherm and the curve of the heats of sorption are in perfect agreement with the same curves of those silicic acid gels that present a so-called "turn".

In silicic acid it is very probable that in the flat piece very fine capillaries are getting filled with water, for absorption of water causes the opaque substance to become transparent again. ZSIGMONDY and ANDERSON¹⁾ pointed out that the radius of these fine capillaries can be calculated from the vapour tension of the water in the flat piece; they then arrived at values of the order of magnitude $1.3 \cdot 10^{-6}$ mm. for the initial part, and 2.6×10^{-6} mm. of the end of the flat piece. And they showed further that when the same silicic acid gel is changed into an alcohol or benzene gel, and the radius of the capillary is calculated from the vapour tension of the alcohol or the benzene, values are obtained for this radius of the same magnitude as in water. This pleads very strongly in favour of the view that the flat middle piece is due to the filling of capillaries, which gradually become slightly wider, hence on micro-porosity.

PATRICK²⁾ repeated these experiments with liquid carbonic acid and liquid sulphur dioxide with silicic acid gel. Then he found, however, much less concordant values for the size of the capillaries; he tried to explain this by the greater thickness of the capillary layer near the critical point.

BACHMANN³⁾, working in ZSIGMONDY's laboratory, also explained the flat middle piece in the isotherm of carbon and water by a system of such fine capillaries. The substance being opaque, it cannot be ascertained if this property becomes stronger in the middle piece.

¹⁾ Zeitschr. f. physikal. Chemie, **88**, p. 191 (1914); ZSIGMONDY, Lehrbuch der Kolloidchemie, 4th edition, p. 219—234.

²⁾ PATRICK, Diss. Göttingen, 1914.

³⁾ BACHMANN, loc. cit.

My experiments lead to the following values for this radius:

$$i_1 = 0.157 \quad h_1 = 0.410 \quad r_1 = 1.24 \times 10^{-6} \text{ mm.}$$

(beginning of the
flat piece)

$$i_2 = 0.362 \quad h_2 = 0.517 \quad r_2 = 1.67 \times 10^{-6} \text{ mm.}$$

$$i_3 = 0.491 \quad h_3 = 0.596 \quad r_3 = 2.13 \times 10^{-6} \text{ mm.}$$

$$i_4 = 0.57 \quad h_4 = 0.65 \quad r_4 = 2.57 \times 10^{-6} \text{ mm.}$$

(end of the
flat piece).

The values found for the radius of the micro-capillaries, are in such close agreement as regards order of magnitude with the values of ZSIGMONDY and ANDERSON, and with those of BACHMANN, that it is astonishing that always *this* order of magnitude is again met with. (The second system of capillaries which BACHMANN thinks that he can derive from his curves, seems questionable to me).

The agreement in the form of the curves for the heats of sorption with their typically flattened piece corroborates that the flat part of the isotherm for carbon and for silicic acid has the same cause.

It is the more striking under these circumstances that BERL and ANDRESS have found that the same carbon which gives a flat middle piece in the isotherm with water, has *a curve without any flat middle piece*, and with a much longer horizontal initial part (for small l) *with organic liquids* (as benzene or methyl alcohol). If the correctness of these experiments is confirmed, they furnish the proof that ZSIGMONDY's explanation, cannot be the true one, at least for carbon. I am, therefore, occupied with a repetition of these experiments, and also with a determination of the heats of sorption.

Since ZSIGMONDY's explanation is inadequate to account for the flat piece in the isotherm and for the flattened piece in the heats of sorption, it is in my opinion natural to see a connection between the deviating form of the isotherm of water and the fact that *water moistens solid bodies, as carbon, much less easily than organic liquids*, as benzene or methyl alcohol, do. We should then have to do in water and carbon with surface adsorption at a surface that is not easily moistened, a phenomenon of which so far only one example has been studied somewhat more closely¹⁾, viz. the adsorption of watervapour to glass-wool which has been thoroughly dried beforehand, investigated by TROUTON²⁾. The glass-wool had been previously

¹⁾ FREUNDLICH, *Kapillarchemie*, 2nd edition, p. 223. Possibly there is solid solution present as a complication in the boundary layer also here.

²⁾ FREUNDLICH, *loc cit.*

treated by drying at 162° over phosphorus pentoxide, and then gave an isotherm with a flat middle piece (possibly even with a faint retrograde piece), which shows a close analogy with the shape of the isotherm for water and carbon. When the glass-wool had been well moistened beforehand, it gave an S-form, as they have been found in mixtures of sulphuric acid and water, and in swelling bodies with water as imbibition-liquid; characteristic is there the beginning with a strongly pronounced horizontal piece for small i , in which region FREUNDLICH's adsorption formula is valid. Similar curves were found by BERL and ANDRESS for the adsorption of those liquids that moisten the carbon well.

This conception might also be able to explain why the adsorption by carbon of water presents such strong hysteresis, whereas that of organic vapours seems to take place without hysteresis. It is, however, possible that solid solution in the boundary layers also plays a part in this¹⁾.

The experiments are being continued.

5. Conclusions.

1. In the investigation of the phenomena of sorption it is insufficient to determine the isotherm of binding; it is necessary to determine at the same time the heat of sorption as function of the quantity of absorbed substance at *the same material*.

2. The examined animal carbon appeared to have an isotherm with an almost flat middle piece, analogous to the isotherm of newly-made silicic acid. The sorption-heat had a course corresponding with this, a flattened middle piece.

3. By assuming that this course is explained by a system of micro-capillaries, I calculate the radius of these capillaries from the isotherm at 1.2 to $2.6 \mu\mu$ (as for silicic acid). That this dimension agrees so closely with that for silicic acid, is somewhat strange and striking.

4. It is, however, doubtful whether this explanation by the assumption of a system of micro capillaries is the true one. It seems probable to me that the difficult moistening of the carbon by water accounts for it.

5. Very striking is the strong hysteresis in the isotherm²⁾.

¹⁾ In the search for possible explanations for the deviating behaviour of *water* at carbon much light was thrown on the subject by conversations with Dr. M. POLANYI.

²⁾ The complicated results of B. GUSTAFER (Kolloidchem, Beihefte, 1922) and HÄLLSTRÖM's experiments (Diss. Helsingfors, 1920) will be discussed in a following paper. Not to lengthen this communication, I confine myself to only mentioning them here.

Chemistry. — “*Volta-Luminescence*”. By Dr. J. LIFSCHITZ. (Communicated by Prof. F. M. JAEGER).

(Communicated at the meeting of June 30, 1923).

§ 1. On the passage of electric currents through Voltaic cells phenomena of light are often observed at the electrodes. This “electrolytic”, or rather this “electrode” light can appear both at the anode and at the cathode, as well on use of continuous current and of alternate current. The nature of the emitted light has seldom been investigated, and then only unsatisfactorily. Consequently so far only little could be said with certainty about the nature of the process. Some researchers (1, 2, 3) have interpreted some of these phenomena of light as reaction luminescence phenomena — hence as belonging to the phenomena of chemi-luminescence. If this should appear to be true, this would be of importance, because, as is known, ionic reaction is hardly ever attended with luminescence (4, 5). Besides the phenomena in question are of importance spectroscopically and electro-chemically. The light emissions under consideration may certainly not be considered as of an exclusively thermal character. For, as earlier experimenters already observed, the phenomenon of light is as a rule the more intense, as electrode and electrolyte have a lower temperature. Often the luminescence only occurs at very small intensity of the current. The spectrum is mostly discontinuous, or it presents at least a maximum of intensity, as is not possible with purely thermal radiation. At any rate an incandescence of the electrode metal can be distinguished with perfect certainty from the luminescence proper. Hence we are justified in distinguishing the phenomena in what follows as “Volta-luminescences”; and it will appear that inter se these are of very different characters, though on the other hand they resemble each other more or less in the following respects:

1. There is mostly a considerable increase of the resistance of the cells, as long as the electrode emits light.
2. Formation of solid or gaseous layers at the luminescent electrode, which sometimes entirely prevent the passage of the current.
3. Often an abnormal course of the electrolysis can be observed.

1. *Cathodic Luminescence.* (WEHNELT interruptor, Chromoscope of v. BOLTON.)

§ 2. The first data about phenomena of light at the anode, as they appear in the WEHNELT-interruptor, were given by WEHNELT (6) himself. VOILER and WALTHER found (7) that much stronger light effects are obtained when the smaller electrode is made cathode, hence when the interruptor is inserted reversely. A very pure spectrum of the electrode metal is then observed, and further some of the hydrogen lines appear. The phenomena also occur when the cell is not inserted as an interruptor, hence without induction coil.

Without taking these observations sufficiently into account, v. BOLTON (8) later described an arrangement which was suitable for spectralanalytic purposes and closely resembled the preceding one. He called this arrangement "Chromoscope". As anode served a thick platinum wire or platinum plate; as cathode he used a platinum wire, or a rod of the metal that was to be examined spectro-analytically. The electrolyte (H_2SO_4 , or better HNO_3 1 : 4) contained in the first case a small quantity of the substance to be examined. When the current is closed by carefully immersing the cathode, very clear and pure spectra of the metals are obtained, which are present as electrode or in the electrolyte, and besides H-lines (especially H_α) and the Na-D-line. v. BOLTON used a potential of 110 Volt; then the strength of the current in his electrolyte-chromoscope amounted to 0,15—0,3 Amp., in his metal chromoscope to 2 Amp.

MORSE (9) investigated the light of the WEHNELT-interruptor more closely. He used an alternate current of a pretty considerable strength, and found that cathode and anode give the same spectrum; the cathodic light was, however, much stronger than the anodic light. He did not observe H-lines. The spectra obtained sometimes resembled the arc-spectrum more closely, sometimes the spark spectrum, without his being able to give a satisfactory explanation of this. There are, however, always characteristic differences between WEHNELT- and spark-spectra, resp. WEHNELT- and arc-spectra. We shall come back to further observations of MORSE later on.

For the investigation of the cathode spectra the arrangement of v. BOLTON is the most suitable; this was still somewhat modified for experiments of longer duration. Fig. 1 represents a simple model of an electrolyte-chromoscope, with which experiments can be made without difficulties. A U-tube is placed within a cooling-jacket; the legs of this tube are closed by two rubber stoppers, in which

the electrodes are fastened. By means of an intermediate piece the two legs are connected with each other and with the water-jet suction-pump, which immediately removes the oxyhydrogen gas formed in the electrolysis. The luminescence is started by the immersion of the cathode, and at the same time the cell is closed air-tight. In the metal chromoscope the tube drawn in fig. 2 comes in the place of the *U*-tube.

In order to photograph the spectra, the light was thrown on the slit of a HILGER spectrograph by means of a small condenser with small focal distance. When Viridin-Inalo plates were used, the exposure had sometimes to be continued from 40 to 150 minutes, because spraying took place. As electrolyte HNO_3 1:4 was generally used; other electrolytes, however, may equally well be used, e.g.

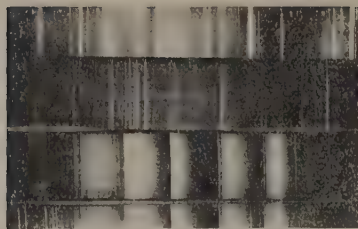


Fig. 1

Fig. 2

diluted or concentrated H_2SO_4 , KOH etc.; this brings about no essential difference as to the nature of the phenomena.

Al-spectra.



Spark.

Electrolytechromoscope.

Metalchromoscope.

Arc.

Cu-spectra.



Spark.

Electrolytechromoscope.

Arc.

Metalchromoscope.



Mg-spectrum in d.electrolytechromoscope

Mg-arcspectrum.

Strontium.



Strong solution.

Dilute solution.

Copper.



160—180 V. 68 min.

< 100 V. 136 min.

Spectra obtained with the electrolytechromoscope.

Fig. 3.

§ 3. In contrast with what was found by MORSE, H-lines (especially H_{α}) were present in the emitted spectrum; further Pt-lines at platinum cathodes. *Apart from this it was stated that electrolyte and metal chromoscope, give totally different spectra*, — a fact which was quite overlooked both by v. BOLTON and by MORSE. When the metal that is to be detected, only occurs in the electrolyte, the spectrum very closely resembles that of the spark-spectrum of the metal. If this same metal is, however, immersed as cathode in pure acid, a spectrum is obtained which agrees closely with the arc-spectrum. As an illustration of these facts, which I could verify repeatedly, some photographs have been reproduced here (fig. 3).

That we are justified in speaking of a general behaviour here, follows for the rest, besides from our own observations (with Mg, Pb, Fe, Wo, Mo, Ta, Al, Cu etc.), also from the data of v. BOLTON and MORSE themselves. If the metal is at the same time in electrolyte and electrode, it is to be expected that a superposition of the two spectra is observed. Since, however, the metal chromoscopes produce more intense phenomena, it is easy to understand that MORSE observed a strong arc-spectrum that is generally superposed by a weak spark-spectrum.

If the chromoscopes are to function normally, a definite current intensity is required in both cases, which though dependent on the adjustments of the apparatus, always remained within the limits indicated by v. BOLTON. With Cu-salt in the electrolyte chromoscope (fig. 1) e. g. 0,4–0,5 Amp. appeared to be required. A greater intensity of the current caused incandescence of the wire, and the disappearance of the luminescence, whilst a weaker current caused the total light intensity to become smaller. As appears from the adjoined photographs, also a selective weakening takes place: some lines losing much more in intensity than the rest. The same effect may also be reached by greatly diminishing the concentration of the metal salt.

In many cases, especially when earth-alkali salts are used, one has the impression that the whole liquid at the cathode is luminescent. This effect is, however, not always found; besides the spectrum was not changed by this. The co-luminescence seems to be caused by still unknown accessory circumstances.

With regard to the mechanism of the emission process it may be considered as an established fact that the cathode is surrounded by a gas envelope. As already VOLLER and WALTER observed, this may be shown simply as follows: when a well-luminescent chromoscope is

first cut out, and then immediately inserted again, the luminescence quickly continues without it being necessary to take the electrode out of the liquid and immersing it again. If, however, we wait a short time after the cutting out, a hissing sound is heard after about 2 or 3 sec., and now the chromoscope is not at once luminescent again when it is inserted. Moreover the experiments of RIESENFELD and PRÜTZER (11) have described, plead still more in favour of the existence of a gas layer. There a small of light arc is formed between cathode and liquid, and I could verify that the same spectral phenomena are obtained as in the chromoscope. On use of Pt- or Ir-cathodes, the metal to be detected being present in the liquid, a spark-spectrum is obtained; when, however, the metal is used as cathode with pure acid, and arc-spectrum.

§ 4. Probably the following idea must be formed about the origin of these cathodic luminescence phenomena. Between electrode and electrolyte there is formed a gas envelope containing hydrogen, water-vapour and some oxygen; within this layer lies almost the whole fall of potential of the cell. The cations not being able to traverse this layer, there a current of rapid cathode rays is formed, which discharge these cations. The discharged metal atoms now get into the gas layer, and are excited to the emission of a spark-spectrum by collision with similar flying electrons.

The spraying of the cathode is greatly promoted by the impact with positive particles. If, as in the metal chromoscope, the current density and the strength of the current intensity are relatively high, also uncharged atoms of the electrode metal get into the gas layer — either because the spraying consists primarily in a scattering of molecular particles, or because locally a sufficiently high temperature arises —, and then an light-arc is formed and hence an arc-spectrum is observed.

If the electrolyte at the same time contains a sufficient number of ions of the electrode- or another metal, a spark spectrum of the second metal can of course appear by the side of the arc-spectrum of the first metal. This is, however, not necessary. Depending upon the nature of the electrode metal, the arc-spectrum is more or less apparent. Thus MORSE showed already that the spectrum of a platinum cathode is intense in solutions of acids and alkalies, but very faint in solutions of earth alkalies, while a strong aluminium (arc-)spectrum appears with an aluminium electrode in almost any electrolyte. The relations that are valid here must, however, still be examined; possibly the greater or less tendency to spraying of

the electrode material is playing here a prominent part. That melting-point and evaporation point of the metal are not decisive, has already been stated by MORSE.

(II) *Anodic Luminescence.*

§ 5. As might be expected, the phenomena at the anode are much more numerous and much more complicated than those at the cathode. Besides gas layers, also layers of solid substance can establish themselves here between electrolyte and electrode, thus causing luminescence. The sparks which appear in valve cells at the limiting tensions (10), have not been examined in what follows.

According to the nature of the emitted light and the cause of the luminescence at the anode, the following typical cases of luminescence can be distinguished.

1. Line- and band-spectra; to a certain extent these are very similar to those at the cathode, but they are generally much weaker.

2. Arc-spectra, equal to those at the cathode, but which can but rarely be obtained, and then only on definite conditions.

3. Generally a yellowish luminescence — which in so far as this can be ascertained, is spectroscopically continuous, — without formation of a layer of oxide or anything of this kind. The anode metal (or the carbon used as anode) gets shiny or bright.

4. For so far as this can be ascertained a continuous emission, with a maximum of intensity in a definite spectrum region; in this case the formation of solid layers at the anode always takes place.

First of all we will give some instances and some further particulars of the phenomena in each of these four classes.

§ 6. 1. Already VOLLER and WALTER record that at an interruptor anode from platinum in sulphuric acid 1:40, they obtained — by the side of the NaD-line — a faint band spectrum. If this cell contained sulphuric acid and also metal salts, the lines of these metals also appeared. The data of these investigators could be fully confirmed; no more than they, did I, however, succeed in determining more accurately the band-spectrum lying in the green¹⁾. The intensity of the phenomenon was, indeed, too small for spectroscopic investigation, though it was always clearly perceptible, also in aqueous potassium hydroxide 1:10, and on use of other anode metals. Special phenomena were obtained on use of platinum anodes in sulphuric acid 1:40, containing at once several metallic salts.

In order to obtain anodic metal lines, greater quantities of metallic salt must in general be dissolved in the acid. Even then mostly a

¹⁾ Very probably these „bands” belong the oxygen spectrum.

few characteristic lines stand out very clearly (e.g. the green Tl-line; the three green Cu-lines). If the acid contains two kinds of metalions, often only one of these kinds of ions can be detected spectroscopically. An example of this is furnished by the following experiment:

A platinum anode was immersed in sulphuric acid 1:40, which contained a sufficient quantity of sulphate of sodium and sulphate of copper. First so much current was passed through that the anode wire became incandescent; then gradually resistance was inserted until the incandescence stopped and the characteristic yellow luminescence appeared. Only a very strong Na-D-line was observed then in the spectroscope. When gradually still more resistance was put in, the yellow luminescence and the Na-D-line became fainter and fainter, and the Cu-lines began to appear (in the green). At a definite terminal voltage green sparks were also immediately to be observed by the side of the yellow sparks at the anode.

It is exceedingly difficult to elucidate the nature of these very faintly luminous phenomena experimentally. It can only be stated that the luminescence appears to be caused by numerous sparks, and that there is undoubtedly a gas-envelope present also here, as already VOLLER and WALTER pointed out. Very probably a similar mechanism is to be supposed here as in LECOQ DE BOISBAUDRAN's "fulgurator". In this apparatus we have a layer of gas and vapour between anode and electrolyte, through which the sparks penetrate.

§ 7. 2. A beautiful and very intense anodic arc-spectrum can be obtained with an iron rod in hot concentrated or diluted sulphuric acid (sp. gr. 1.80 and H_2SO_4 1:4); less easily by means of tungsten anodes in the same medium. Then the temperature of the anodes is pretty high; the colour of the emitted light is a brilliant blue. The tension in these experiments was 225 Volts. The emission did not appear until the luminescence described under 3 had been observed for a shorter or longer time. We shall, therefore, have to return to the said phenomenon presently.

3. A very peculiar light phenomenon is observed when the current is closed by immersion of a carbon- or metal-anode in concentrated or diluted sulphuric acid. The carbon then gets covered by a beautiful yellow mantle of light, which continues to persist for a long time; the carbon surface gets smooth, carbon powder and superficial impurities are removed. Metal anodes present an analogous behaviour, as was by observed by v. BOLTON (8), to whom we owe a method by this procedure for polishing and cleansing carbon electrodes. (14).

I have been able to corroborate the validity of this experimenter's results in every respect — both on use of concentrated and of diluted sulphuric acid. A digressing behaviour is shown only by typical valve metals (e.g. Al and Ta). These emit a white or bluish light.

For so far as could be ascertained, the spectrum of the yellow light is continuous; often the Na-D-line is still to be observed. After the experiment the electrodes surface is bright and smooth, but the electrode-diameter is mostly slightly diminished. The white light from valve metals is continuous, but on the boundary electrode-electrolyte-air sparks often appear then, which certainly emit line-spectra.

The terminal voltage during the yellow luminescence (in Cu, Fe, Mo, Wo, Ni, C) is about 100 Volts, the intensity of the current some tenths of an Amp., i.e. on use of wire-electrodes of a diameter of some mm., which were immersed 1—2 cm. deep. The temperature of concentrated sulphuric acid then rises very rapidly to the boiling-point, that of diluted sulphuric acid (smaller intensity of current) somewhat more slowly. When once the boiling-point temperature has been reached, the colour suddenly changes from goldish to brilliant blue; at the same time the current is reduced to less than 0,1 Amp., the terminal voltage rising to the total value available (225 Volts). Then the well known arc-spectrum of iron or tungsten is seen in the spectroscope. This experiment is very suitable for demonstration. Analogous phenomena can most probably also be obtained in other metals, though less easily.

§ 8. The appearance of an anodic arc of light particularly at hot anodes, is, indeed comprehensible; the yellow luminescence is, however, less easy to understand. A purely thermal emission of the metal cannot be supposed. Nor can there be any question of a reaction luminescence, since the light always possesses the same colour, no matter what anode material is used. VON BOLTON suggested that the anode gets covered with "a yellow incandescent" oxygen mantle. In fact oxygen can be brought to an emission of a yellow continuous light by an electric current at higher pressure (13). At lower pressure a maximum of intensity in the green or yellow green occurs in this continuous spectrum. It may, therefore, be assumed as very probable that our electrodes are surrounded by a mantle of oxygen generated electrolytically, in which the gas is brought electrically to light emission under pretty high pressure. At higher temperatures the pressure in this oxygen layer must diminish, perhaps the layer must become quite unstable, and finally conditions are reached which give rise to a metal arc of light.

§ 9. 4. Anodic light emission has often been observed during electrolyses, when an insoluble or sparingly soluble reaction product is formed at the anode. This product can then form either a solid layer firmly attached to the anode, or a layer that gets more or less easily detached.

The former can often be observed in valve cells. Already below the limiting tension a dullish white light may be seen at the valve anode (10), which becomes pretty intense under definite circumstances, (e.g. with Al-anodes in borax solution, Ta in diluted alkali or carbonate solution). With this emission of light should also be classed the emission of light of magnesium anodes in diluted alkali (15).

In all these cases the potential rises to the maximum value available, the passage of the current is almost entirely prevented. The luminescence begins very soon after the closure of the current, often with periodic oscillations of the intensity during the first minutes, and then continues to persist till the current is broken. The light emission is, however, generally soon prevented, when electrode or electrolyte are heated by the weak current that continues to pass. In prolonged experiments it is, therefore, necessary to ensure good cooling.

The light, which is almost always a dullish white, sometimes more greenish or bluish, appeared to be continuous on spectroscopic investigation.

It is also noteworthy that with magnesium anodes the maximum of light intensity is reached in potassium hydroxide 1:100; a very strong luminescence is also obtained by using an ammoniac solution of di-sodium phosphate instead of the hydroxide. In this medium also zinc anodes produce an exceedingly beautiful light emission, a borax solution being the most suitable electrolyte with aluminium. But also with aluminium and with tantalum diluted alkali hydroxide solution etc. can be used.

In these processes the electrolyte is covered by an adhering layer of the oxide or of another insoluble anode product, as this was already shown by other experimenters. The generality of such phenomena is brought out by the fact that always new observations of the kind described are being communicated (cf. e.g. 1a).

But also when no direct valve actions are to be observed, such phenomena of light are nearly always found when at the anode a sparingly soluble product is found. To these belong, among others, the following phenomena of luminescence which have partly already been known for some time:

Electrolyte	Phenomenon
KJ aq, saturated	a bright luminescence at anodes of Cd, Hg, Pb.
H ₂ SO ₄ conc.	" " " " " " Pb, Al, Ta; Mg gives a short flash; at Cd anodes there is seen a ring of light, which moves up and down.
KOH aq, strong	Fe (a bright luminescence, but which cannot very easily be examined on account of strong foaming), Ni (very slight intensity of the current).
Na ₂ HPO ₄ NH ₃ aq	Cu gives a circle of sparks.

Exceedingly intense is the luminescence at an Hg-anode in saturated KI-solution at sufficient density of the current. The bright anode-surface is covered with a thin layer of mercury iodide immediately after the closure of the current, and then begins to emit a golden light. After a short time the intensity of this light reaches a maximum, and then diminishes again. By renewal of the mercury surface, either by stirring or by allowing the mercury to overflow from a funnel-shaped anode vessel, etc. the luminescence can be restored with full intensity.

In agreement with former experimenters (2) the spectrum of the emitted light was found to be continuous, with a maximum of the intensity in a definite spectral region. WILKINSON (2) has pointed out that the colour of this light also agrees with that of the light emitted by the anode product in question, when it is bombarded by cathode rays.

§ 10. It is exactly these kinds of luminescence that are very often considered as reaction luminescence (chemi-luminescence). Formation or decomposition of the anode products were thought to be accompanied by a luminescence which could reach a considerable intensity with sufficient reaction velocity¹). BANCROFT (1) and his pupils, also WILKINSON (2) have endeavoured to give support to this view. In the course of our own observations on comparison with those of other investigators it appears, however, that this conception is untenable.

In the first place it can be established that all the phenomena described in this chapter, are related. And this not only because they appear to be of the same nature spectroscopically, but also because their occurrence always appears to be bound to the formation of sparingly soluble or insoluble anode products.

¹) On this conception compare (5).

Premising this, it may be inferred from a pretty great number of reasons that a conception of these luminescence phenomena as reaction luminescence phenomena must be considered as erroneous.

In the first place with this view of the matter it cannot be explained why only formation of insoluble products gives rise to luminescence. It can, indeed, be predicted that the probability of anodic luminescence and its intensity will be the greater as the anode-product dissolves with the greater difficulty. For it appears in particular that on formation of readily soluble anode-products, luminescence never seems to be observed.

Nor can the considerable increase of intensity of the luminescence at low temperature (hence at smaller reaction velocity) be accounted for on the ground of the said conception. For with valve anodes the luminescence is by no means most pronounced on particularly strong anode-reaction, but only when the excluding layer is as stable and homogeneous as possible, and is attacked as little as possible by the electrolyte. Thus magnesium emits the brightest light in *diluted* KOH, aluminium in borax solution, which would certainly be unaccountable in the case of real "chemi-luminescence". A magnesium anode is particularly strongly attacked by diluted sulphuric acid, though all the same, there is no luminescence at all to be observed.

Moreover it remains inexplicable how anodes which are rapidly covered by an insoluble layer, yet continue to emit light. It might much sooner be expected in this case that the light would cease after the formation of a covering layer. But this is by no means observed in the majority of the cases.

Finally the increase of light intensity after the closure of the current, as is particularly clearly observed with mercury anodes in KI-solution, is unaccountable in a reaction luminescence. For, how a certain quantity of reaction products would be able to increase a direct chemi-luminescence, is not clear. Nor can periodic and rhythmic light emissions (Cd in KI-solution, Mg immediately after the closure of the current) be accounted for in this way.

§ 11. The only conception which can be brought to harmonize with all the experimental facts, is in contrast with the conception discussed just now, in my opinion the following: at once after the closure of the current a layer of reaction products is formed at the anode, which hampers the passage of the ions to the anode, or renders it impossible. Then the electric discharge of these ions takes place (at sufficiently high potential) under the influence of split off

anionic electrons, which fly through the anode layer with strong acceleration. By this the matter in this layer is brought to luminescence in the same way, hence with emission of the same spectrum, as this would happen by means of cathode rays. If the layer becomes too thick, higher potentials will be required to bring about a passage of the current, and finally current could only pass in certain cases when the layer is traversed by sparks (limiting tension with anodes). When on the other hand the layer is attacked by the electrolyte in some way or other, it is very well possible that also the light emission at the anode can vary locally, and in particular the periodic oscillations of the intensity along the anode become possible. Increase of temperature will always hamper the luminescence, either because the solubility of the anode product is in general increased by it, or because the layer is rendered less stable by it in mechanic respect. If the anode layer has little mechanical stability in itself (e.g. mercury iodide), a certain minimum current density will be required to form a coherent layer with sufficient velocity, and to allow this to continue to exist, in spite of continued decomposition.

By this conception also the analogy between the anodic and cathodic luminescences is clearly brought out.

Summarizing we may say that also in these anodic luminescence phenomena, as this was earlier shown for ordinary chemi-luminescence (5), not the anode-reaction in itself takes place with light emission.

It must rather be admitted that first reaction products are formed which are brought to emission, in this case by means of the electric energy of a source of current outside the system examined ¹⁾. Hence there is no question of an ion reaction, which takes place with light emission, and of a departure from the general rule that it is just these reactions, which proceed practically with infinite velocity, that are never accompanied by a light-emission.

The above considerations show further that VOLTA-luminescence occurs very frequently, but also that it can be of a very different character. On further investigation of these phenomena it will be necessary to distinguish these kinds of VOLTA-luminescence scrupulously. The present investigation may be considered as a first attempt at reconnoitring the ground in this respect.

¹⁾ In cases of common chemi-luminescence the reaction itself furnishes the energy necessary to excite to light emission some of the kinds of molecules present in the system. (see 5).

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Physiology. — „*Is Caesium Radio-active?*” By Prof. H. ZWAARDEMAKER, W. E. RINGER and E. SMITS.

(Communicated at the meeting of June 30, 1923).

Up to the present potassium and rubidium are the only elements in the series Li, Na, K, Rb, Cs, which have been proved to be radio-active. It has often been suspected that caesium also possesses a slight radio-activity, but thus far this is not certainly known. E. RUTHERFORD¹⁾ simply remarks that caesium is barely radio-active and ST. MEYER and E. VON SCHWINDLER²⁾ suggest that radio-activity may possibly exist, but the penetrating power of the rays emitted is so low that it does not reach beyond the limits of the substance. We know for certain that commercial preparations of caesium exert no photographic action, even in exposures for months. Neither could one of us³⁾ detect in carefully purified caesium preparations any ionization of the air of a flat ionization-chamber.

It is a fact, however, that biologically caesium exerts in many cases an influence similar to that of potassium and rubidium. This influence was already known to SIDNEY RINGER⁴⁾ and has, moreover, been purposely studied by one of us.⁵⁾ After an unsuccessful effort in winter we succeeded in the summer of 1917 in keeping hearts of coldblooded animals beating on a dosis of caesium-chloride that only slightly differed from the usual potassium-dose. It appeared that potassium-, rubidium- and caesium-chloride could be used promiscuously, but that a much larger quantity of caesium had to be applied for a toxic effect. With regard to uranium, thorium, radium, and radium-emanation it behaved antagonistically, which was afterwards also confirmed by Miss L. KAISER⁶⁾.

Here, then, a contrast manifested itself. Physically well-purified caesium-compounds are to be considered as non-radio-active, whereas

1) E. RUTHERFORD in MARX's Hdb. der Radiol. Bd. II S. 531, 1913.

2) ST. MEYER und E. v. SCHWINDLER, Radioaktivität, 1916 S. 428.

3) W. E. RINGER, Arch. néerl. de Physiol. t. 7 p. 434, 1922.

4) S. RINGER, Journal of Physiol. Vol. 4 p. 370, 1883.

5) H. ZWAARDEMAKER en C. DE LIND VAN WIJNGAARDEN, K. Akad. v. Wetensch. 27 Oct. 1917, Proc. vol 20 p. 773.

6) L. KAISER. Arch. néerl. de Physiol. t. 3 p. 587, 1919.

biologically a well-proportioned dosis of caesium behaves like the radio-active elements potassium and rubidium.

To elucidate this we undertook an experiment with preparations of various origin. They were carefully purified and examined physically and biologically before and after the purification.

By a physical inquiry we tried to determine the ionization-power of the perfectly dry caesium-salt in a flat, air-tight ionization chamber. The salt had been spread evenly on a copper dish of 30 cm. diameter.

The dish was isolated with amber and charged to constant potential of 500 volts by a battery of small accumulators. $3\frac{1}{2}$ c.m. above the salt layer was a copper disc also of 30 cm. diameter, which was connected with a pair of quadrants of a sensitive electrometer. The "needle" of this electrometer was maintained at 40 volts.

A uranium-unit of Mc Coy of 50 square m.m. showed with this arrangement a deflection of 100 scale-divisions in about 2 minutes; a layer of dried potassium-chlorid in 5 minutes about 50 scale-divisions ¹⁾.

Our caesium-chloride preparations yielded widely differing results, of which a survey is best obtained by a comparison with the ionization power of potassium *ceteris paribus*.

Activity	Impure	Pure
CsCl of E. DE HAËN	1/6 of the act. if potassium	1/37 of the act. of potassium
CsCl of MERCK	1/10 " " " "	inactive
CsCl of KAHLBAUM	1/37 " " " "	1/80 of the act. of potassium
CsCl of POULENC fr.	1/37 " " " "	1/77 " " " "

. The biological examination was carried out with an isolated frog's heart (ventricle + right auricle suspended to a SYMES cannula with an overflow, so that the pressure could never exceed 5 cm. of water. Three Mariotte-flasks with a cock-system provided a means of per-

¹⁾ We see, then, that in this flat ionization chamber the ionization power of potassium (beta-radiator) is 7000 times weaker than that of uranium (alpha-radiator). This ratio will be quite different in a high ionization-chamber. RUTHERFORD (p. 528) estimates the ionization power in the ordinary ionization-chamber at $\frac{1}{1000}$ of the beta-radioactivity of uranium. The beta-radioactivity of uranium in its turn rests on uranium X, with which the uranium of the ordinary preparations is in equilibrium.

fusing the heart alternately with Ringer-solutions of various composition. First we determined the minimum dosis of potassium-chloride that the individual heart required, after which it was perfused with a RINGER-solution, without potassium until it came to a standstill. After ten minutes, in which interval we ascertained that no latent automaticity existed, we proceeded to caesium perfusion. We determined in succession the minimum-, the optimum- and the maximum-doses. The dosage was gradually increased with the greatest care. By means of an air-injector, such as was used by LOCKE and ROSENHEIM, the same $\frac{1}{2}$, or 1 Liter of circulating fluid was sent round. The fluid that went through the heart was thus loaded with as much oxygen as is soluble in a weak salt-solution.

The dosis of potassium-chloride and of caesium-chloride that proved just sufficient to make the heart beat regularly, was considered as the minimum dosis; as optimum dosis we took the one which yielded the greatest frequency and maintained it. It was difficult to find the maximum-dosis, because an increase in the caesium dosage brings on an inconvenient negative inotropism.

We then considered as highest practicable dosis the one which produced lytic symptoms of cessation of contractility. Strictly the maximum dosis lies somewhat higher. Meanwhile the caesium has penetrated deep into the heart-cells, for it takes hours before a heart can be deprived of the profusion of caesium and before its action can be arrested by a RINGER-solution that contains neither potassium nor caesium.

A survey of our results can again be best obtained by an inter-comparison of caesium and potassium.

Minimum-dosis of the impure preparations.

CsCl of DE HAËN	8.7 \times KCl-dosis
CsCl of MERCK	5.3 \times KCl-dosis
CsCl of KAHLBAUM	4.9 \times KCl-dosis
CsCl of POULENC fr.	4.1 \times KCl-dosis

The minimum-, optimum-, and highest practicable doses are, for the impure preparations in milligrammes of caesium-chloride per Liter on an average in the ratios of:

1194 : 1538 : 1998.
min. opt. highest pract.

Of the purified doses the quanta must be much larger:

Minimum-doses of the purified preparations.

CsCl of DE HAËN	$9.5 \times$ KCl-dosis
CsCl of MERCK	$19.4 \times$ KCl-dosis
CsCl of KAHLBAUM	$7.2 \times$ KCl-dosis
CsCl of POULENC fr.	$12.3 \times$ KCl-dosis

The minimum-, optimum-, and highest practicable doses are for the purified preparations of caesium in milligrammes of caesium-chloride per Liter, on an average in the ratios of:

1678 : 2760 : 4134.
min. opt. highest pract.

When comparing impure and pure caesium we obtained the following mean results:

	Impure CsCl	Pure CsCl
in minimo	$5.5 \times$ min. KCl	$10.7 \times$ min. KCl
in optimo	$7.1 \times$ " "	$17.7 \times$ " "
highest pract.	$9.2 \times$ " "	$26.5 \times$ " "

So we see that in minimo the quantity of pure caesium must be from 2 to 3 times larger than that of impure caesium.

On the 16th of May 1923 it appeared that of the preparation, purified to such a degree that no radiation whatever could be demonstrated for a given heart, in minimo 39, in optimo 47 and as highest practicable dosis 58 grs. had to be added per Liter of circulating fluid. It is obvious that in such cases the quantities of NaCl had to be largely diminished in order to prevent hyper-isotonia.

One of us has set up for the radio-active substitutes of potassium a working-hypothesis, viz. that in general isolated organs require so much of a radio-active element in their physiological circulating liquid as is necessary to generate per second the emission of a number of ions that is equal for all substitutes. This hypothesis can be expressed in a logarithmic graph.

In such a graph rubidium and caesium cannot be taken up directly, since we do not know how many ions these substances emit per

second, so that no place can be assigned to them on the axis of the abscissae. When, however, the minimum-, and the maximum-

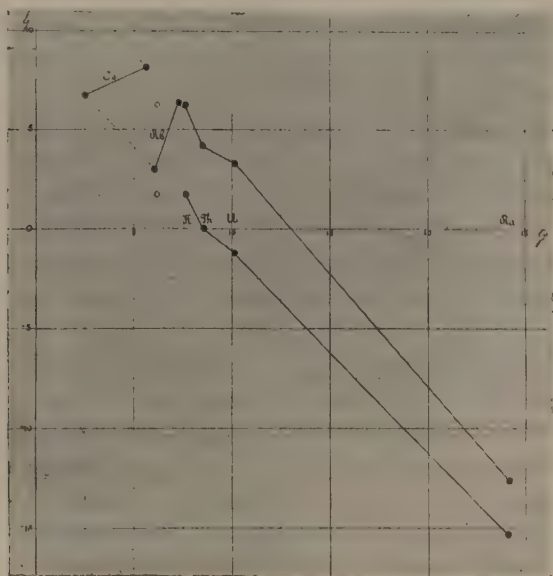


Fig. 1.

dosages are known, a place may be found for them on the axis of the ordinates, and when assuming the law to hold good also for these substances, their hypothetical place on the axis of the abscissae may be determined by erecting a perpendicular. We have plotted the graph accordingly and thus given a value for rubidium as well as for caesium. We know then the presumable number of ions that will be emitted under the given premisses per gram and per second. For our pure preparation of caesium it appears to be 55 per gram and per second. With such a small number of ions we can expect a photographic effect only after 9 years. It is easy to understand, therefore, that up to the present endeavours to produce any effect of caesium upon a sensitive plate, have not been successful.

The 55 ions per gram and per second that, according to the hypothesis of the corpuscular equivalence, should belong to pure caesium, cannot really belong to the caesium as such, but must be due to the impurity of the commercial preparation, which had been removed from the caesium in the following way:

Addition of copper sulphate; perfusion of sulphureted hydrogen for $\frac{1}{2}$ hour; after 24 hours removal of the precipitate of copper

sulphide by filtration; removal of the residue of sulphureted hydrogen by boiling the filtrate.

A second precipitate is generated by adding to the filtrate some drops of ferro-chloride solution and afterwards an excess of ammonia; this precipitate of iron hydroxyd is filtered off again after some hours; this process is repeated three times.

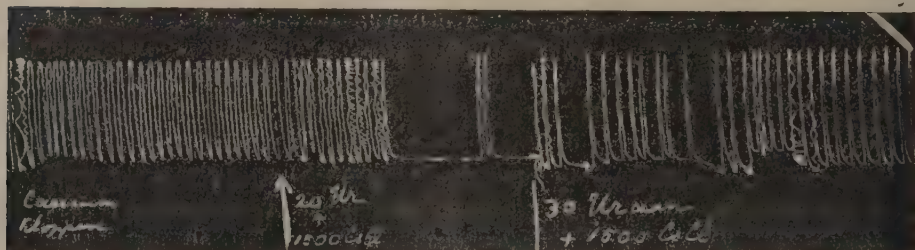
Lastly a third precipitate is generated by adding barium chloride at boiling heat; next day the precipitate is filtered off; this process is repeated under an excess of sulphuric acid, so that all the barium is precipitated; now the filtrate contains a small amount of caesium sulphate over and above all the original caesium chloride.

This procedure serves to remove a heavy radio-active element, which is left behind in the precipitate.

Originally the caesium-salts we used contained some of this impurity. If the dosis is high enough then there will be enough of the impurity to produce a biological action such as we may expect of a radio-active substance.

This biological action has the nature of a beta-radiator as is obvious from the antagonism of our caesium to uranium. Miss L. KAISER has recorded some instances of Cs-U-equilibria.

We annex a recent instance.



kloppen = beat

Fig. 2.

A frog's heart beats initially on a Ringer solution, which contains per Liter instead of potassium 10 mgr. of uranyl nitrate. By adding to this solution a quantity of 1500 mgrms of Caesium-chloride a radio-physiological equilibrium is engendered between the alpha-radiator uranium and the beta-radiator caesium. A standstill corresponds with this equilibrium in which there is not even latent automaticity. However, directly when we increase the quantity of caesium, a caesium beat is developed. Another equilibrium will then again be called forth by increasing the quantity of uranium, which now is on a higher level, because more has been taken of the two

components. Finally a larger amount of uranium restores the heart's beat.

Considering that besides radio-active, also non-radio-active paradoxes occur, (NOYONS, BUSQUET) no conclusive value can be ascertained in the easily generated, transient standstills when passing from a uranium liquid to a caesium liquid and vice versa. It is different with the equilibria, which can only be interpreted radio-physiologically. This is most evident with the higher equilibria in which each of the components, co-exist in the mixture in quantities that undoubtedly surpass the threshold-concentration.

Our inquiry, then, is to the following effect:

1°. the impurity that imparts to the commercial preparation of caesium a feeble radiating power, is presumably a heavy radio-active element.

2°. the biological action of the impurity has the nature of a beta-radiator.

Hydrodynamics. — “On the resistance experienced by a fluid in turbulent motion”. By J. M. BURGERS. (Communicated by Prof. P. EHRENFEST).

(Communicated at the meeting of May 26, 1923).

§ 1. *Introductory remarks.*

The problem which is discussed in the following lines is to search for a method to calculate the resistance experienced by a fluid in turbulent motion. A definite solution has not been arrived at; a first attempt only is given.

As is generally known, in most cases the motion of a fluid through a straight cylindrical tube or channel is not in parallel lines with a constant velocity along each line. On the contrary it is usually very irregular: the velocity of a particle changes its value and its direction continually, and particles situated very near to each other have very different velocities, whereas there seems to be no definite law governing these deviations. This type of motion is called *sinuous* or *turbulent*, as distinguished from the *streamline* or *laminar* motion, which occurs at low velocities only. In studying turbulent flow the conception of the *mean motion* or *principal motion* has been introduced by various authors. This mean motion is obtained if in every point of the space occupied by the fluid the mean value of the true velocity with respect to time is determined, and then the steady motion is imagined the velocities of which are equal to these mean values. The true motion may be described as the resultant of the mean motion and of a fluctuating *relative motion*. The mean velocity of the latter is zero ¹⁾.

A turbulent flow usually experiences a high resistance, which is approximately proportional to the second power of the velocity of the mean motion. If the law of resistance is written:

$$\text{loss of pressure per unit of length } J = C \frac{\rho V^2}{d},$$

¹⁾ In connection with the distinction between mean motion and relative motion the reader is referred to: H. A. LORENTZ, *Turbulente Flüssigkeitsbewegung und Strömung durch Röhren*, Abhandl. über theoretische Physik I (1907), p. 58—60.

in which formula V represents the mean velocity (i.e. the volume of fluid which in unit of time flows through a section of the tube, divided by the area of that section), d the diameter of the tube, and ρ the density of the fluid, then C is called the coefficient of the resistance, and appears to be a function of the characteristic number introduced by REYNOLDS: $R = \frac{Vd\rho}{\mu}$ (μ is the coefficient of viscosity of the fluid). The value of C for different cases is given in textbooks; as an example may be mentioned:

- a. for rough walled tubes C is approximately independent of R ; however, it is a function of the roughness;
- b. for very smooth tubes of circular diameter:

$$C = 0,1582 R^{-\frac{1}{4}}.$$

The greater part of the theoretical investigations on the turbulent motion treat the problem: how does it originate? ¹⁾ An explanation of the increase of resistance which accompanies the appearance of the turbulent state of flow has been given by REYNOLDS and LORENTZ ²⁾. More than once it has been remarked that this problem is one of statistical nature ³⁾. The resistance experienced by the fluid and indicated by our measuring apparatus is a mean value. It is possible that such a mean value may be calculated sufficiently approximate without an exact knowledge of the fluctuating and never exactly returning relative motions.

In the following lines a preliminary attempt is made to determine the value of the resistance and to explain the quadratic law. In the first part (paragraphs 2 and 3) two equations given by REYNOLDS and LORENTZ are discussed and put into such a form that immediately appears what quantities are wanted in order to calculate the resistance. In the second part (paragraphs 4 and 5) a simple idealized "model" of the turbulent flow is constructed which allows these quantities to be determined.

Instead of the flow through a tube or channel a more simple

¹⁾ Comp. f. i. R. von MISES, *Elemente der technischen Hydromechanik* I (1914) p. 57 and H. BLASIUS, *Mitt. über Forschungsarbeiten*, herausgeg. vom V. D. I., Heft 131 (1913).

²⁾ Cf. F. NOETHER, *ZS. für angew. Math. u. Mechanik* 1, p. 125, 1921.

³⁾ O. REYNOLDS, *Scientific Papers* II, p. 575—577;

H. A. LORENTZ, *l.c.* p. 66—71.

⁴⁾ Among others by TH. VON KÁRMÁN at a lecture at the "Versammlung der Mathematiker und Physiker" in Jena 1921; comp. a remark in the *ZS. für angew. Math. u. Mechanik* 1, p. 250, 1921.

type has been chosen: the motion of a fluid between two parallel walls, one of which has a translational motion in its own plane with the velocity V with respect to the other, while the distance between the two walls has the constant value l (comp. fig. 1). To ensure this motion forces of magnitude S per unit of area must be applied

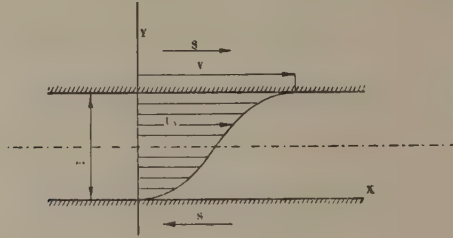


Fig. 1.

to the walls in opposite directions. The tangential force between any two adjacent layers of the fluid has the same value S . The law of resistance will be written:

$$S = C \rho V^2 \dots \dots \dots (1)$$

The coefficient C is a function of REYNOLDS' number:

$$R = \frac{V l \rho}{\mu} \dots \dots \dots (2)$$

For small values of R the motion is laminar, and the value of C is easily seen to be:

$$C = \frac{1}{R} \dots \dots \dots (3)$$

If the value of R is high, the motion becomes turbulent, and C decreases much slower. There do not exist any direct measurements for this case of motion; however, the arrangement of the experiments made by COUETTE comes very near to it¹⁾. According to this author we may expect a formula of the following type:

$$C = c_1 + c_2 R^{-1} \dots \dots \dots (4a)$$

Investigations by VON KÁRMÁN on the law of decrease of the mean motion in the neighbourhood of a smooth wall²⁾ point to:

$$C = 0.008 R^{-1/4} \dots \dots \dots (4b)$$

¹⁾ M. COUETTE, Ann. de Chim. et de Phys. (6) 21, p. 457, 1890.

²⁾ TH. VON KÁRMÁN, ZS. für angew. Math. u. Mechanik, l.c.

The equations (8) and (9) are substantially the same as the formulae (36) and (46) from LORENTZ' paper l.c. above, only simplified according to the conditions of the problem before us.

Now firstly $\frac{dU}{dy}$ will be eliminated from eq. (9) by the aid of (8):

$$-S \int_0^l dy \varrho \bar{u}v = \int_0^l dy \{ \varrho^2 (\bar{u}v)^2 + \mu^2 \bar{\zeta}^2 \} (10)$$

Secondly by integrating (8):

$$\mu V = Sl + \int_0^l dy \varrho \bar{u}v (11)$$

This equation allows the elimination of S from (10):

$$\frac{\mu V}{l} = \frac{\int_0^l dy \{ \varrho^2 (\bar{u}v)^2 + \mu^2 \bar{\zeta}^2 \} - \frac{1}{l} \left(\int_0^l dy \varrho \bar{u}v \right)^2}{-\int_0^l dy \varrho \bar{u}v} \left. \right\} . . (12)$$

In order to simplify the equations we may introduce undimensioned variables by means of the formulae:

$$x = lx', y = ly'; u = Vu', v = Vv'; \zeta = \frac{V}{l} \zeta' . . (13)$$

If now in the following equations the accents are omitted again, we obtain:

$$\frac{1}{R} = \frac{\int_0^1 dy (\bar{u}v)^2 - \left(\int_0^1 dy \bar{u}v \right)^2}{-\int_0^1 dy \bar{u}v} + \frac{1}{R^2} \frac{\int_0^1 dy \bar{\zeta}^2}{-\int_0^1 dy \bar{u}v} \left. \right\} . . (14)$$

and by the same substitutions, from (11):

$$\frac{S}{\varrho V^2} = - \int_0^1 dy \bar{u}v + \frac{1}{R} (15)$$

The equations take a very simple form if the following abbreviations are used:

$$\left. \begin{aligned} - \int_0^1 dy \, \overline{uv} &= \sigma \\ \int_0^1 dy \, (\overline{uv})^2 &= (1 + \tau) \sigma^2 \\ \int_0^1 dy \, \overline{\xi^2} &= \kappa \sigma \end{aligned} \right\} \dots \dots \dots (16)$$

It will be easily recognized that the three quantities σ , τ and κ are all of them essentially *positive*.

The equations (14) and (15) now reduce to:

$$\underline{\sigma\tau + \frac{\kappa}{R^2} = \frac{1}{R}} \dots \dots \dots (17)$$

and:

$$\frac{S}{\rho V^2} = C = \sigma + \frac{1}{R} \dots \dots \dots (18)$$

Formula (17) will be denoted as the *principal equation*.

§ 3. Discussion of the principal equation.

Equation (17) shows first of all that an increase of the velocity V of the mean motion cannot be accompanied by a proportional change of the relative motion: in this case σ , τ and κ would remain constants, whereas R increases, which would violate equation (17).

If the value of R is given, (17) gives a condition to be fulfilled by the relative motion. If a certain type of relative motion, fulfilling this condition, accompanies the mean motion, the latter will experience a resistance determined by the value of C , calculated from (18). Now the problem arises: can we find admissible values of the quantities τ and κ , without an exact knowledge of the true relative motion? If τ and κ are known, (17) gives σ (i.e. in some measure the relative intensity of the relative motions), and (18) gives the resistance coefficient. If we look at the application of statistical methods in the dynamical theory of gases, we should expect that for high values of R (which mean a fully developed state of turbulence), it may be possible to calculate τ and κ in the following manner: firstly we determine all kinds of relative motions which fulfil eqq. (6) and (7); secondly we admit that all these motions may be present independently of each other, their weights being governed

by some law of probability, or by a maximum- or minimum-condition. Then the mean values are calculated for this assembly.

Prof. VON KÁRMÁN from Aix-la-Chapelle pointed out to me that before trying to find a condition governing the weight of the different types of motions, it would be advisable at first to search for the *maximum value* of S , or of σ . In this way a higher limit for the resistance of turbulent flow would be found.

That a maximum value exists may be shown thus:

From (17) it is deduced that σ may become great (i.e. especially: great as compared to $\frac{1}{R}$) only if $\kappa < R$ and if τ becomes small.

The value of τ is determined by the distribution of the values of \overline{uv} over the interval $0 < y < 1$. Only if \overline{uv} assumes a constant value throughout this interval, τ can attain its minimum value 0. However, \overline{uv} cannot be a constant everywhere, as u and v decrease to 0 in the neighbourhood of the walls. Hence we will obtain the smallest possible value of τ if \overline{uv} has a constant value throughout the whole region with the exception of two very thin layers along the walls, in which layers $|\overline{uv}|$ decreases to zero. If the thickness of these "boundary" layers is represented by ε , τ will be of the same order of magnitude as ε , hence with a numerical constant c_1 :

$$\tau = c_1 \varepsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

In the boundary layers $\frac{\partial u}{\partial y}$ and ζ will be of the order of magnitude ε^{-1} , and so $\bar{\zeta}^2$ will be proportional to ε^{-2} . Hence if this intensive vorticity occurs in the boundary layers only:

$$\kappa = c_1 \varepsilon^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Now equation (17) gives:

$$\sigma = \frac{1}{c_1 \varepsilon R} - \frac{c_2}{c_1 \varepsilon^2 R^2}$$

This expression attains a maximum value if:

$$\varepsilon = \frac{2c_2}{R} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The thickness of the boundary layer appears to be inversely proportional to R . The value of σ becomes:

$$\sigma_{\max} = \frac{1}{4 c_1 c_2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

It appears that σ takes a value which is independent of R ;

according to (18) C approximates to the same constant value, and thus according to (1) the *quadratic law* of resistance is obtained.

This reasoning is in many respects vague, and it does not admit of a determination of the values of c_1 and c_2 . It only shows that the particles of fluid with high values of the vorticity $|\xi|$ must be concentrated along the walls. To get a more definite result it is necessary to develop a picture of the structure of the turbulent motion. Two ways may be followed: we may try to analyze the possible motions into a sum of elementary functions (goniometrical or others) in a manner analogous to a series of FOURIER; or we may imagine the motion to be built up from an assembly of individual vortices (vortex filaments with their axes perpendicular to the plane of $x-y$), distributed in some way or other throughout the fluid. In the calculation of the critical value of R (i.e. the value at which the turbulence occurs for the first time) analogous methods have been used: REYNOLDS, ORR and other writers have directed their attention to disturbances which are propagated in a periodic way through the whole fluid; LORENTZ at the other hand has studied the disturbance caused by a single vortex ¹⁾.

The statistical treatment of such an assembly of elementary motions is very difficult on account of the circumstance that every elementary motion is damped by the action of the viscosity. At the other side the mutual actions between the elementary motions (brought forth by the quadratic terms in the equations of hydrodynamics) and the influence of the mean motion continually generate new motions. From the formula given by LORENTZ it follows that types of motion for which $\iint dx dy uv$ is negative, are intensified by the action of the mean motion. Hence a mean stationary state can exist, in which every elementary motion changes continually its intensity and its phase (or its position, if it is an individual vortex), but in which every one of these motions has a constant mean intensity. It is obvious that for the greater part, if not exclusive, these will be types of motion for which $\iint dx dy uv < 0$.

The statistical problem will not be attacked here. On the contrary a simple type of turbulent motion will be studied in the following paragraphs, built up from an assembly of elliptic vortices, all of them having the same configuration, but having different dimensions.

¹⁾ O. REYNOLDS, l.c. p. 570;

W. MC. F. ORR, Proc. Roy. Irish Acad. 27, p. 124—128, 1907;

H. A. LORENTZ, l.c. p. 48.

If they are distributed over the fluid in a certain way, with an appropriate distribution of intensities, it will appear that it is possible to make τ very small, without making the value of κ surpass that of R . It further appears that in the choice of the dimensions of the vortices an element remains arbitrary, which element may be adjusted in such a way that σ takes a maximum value.

§ 4. LORENTZ' *elliptic vortex*.

It has been shown by LORENTZ that we can obtain a simple type of motion which obeys the conditions (6) and (7), and for which $\iint dx dy uv < 0$, by considering a vortex in which the particles of the fluid describe elliptic paths¹⁾. Geometrically this motion can be deduced from that in a circular vortex by a lateral compression. In the circular vortex the fluid moves in concentric orbits with the angular velocity ω , which is a function of the radius r of the orbit. At the outer boundary of the vortex ω has the value zero, whereas in its centre ω and $\frac{d\omega}{dr}$ have finite values. LORENTZ takes for ω a BESSEL function of r ; in order to obtain simpler formulae in this paper an algebraic function will be taken.

The construction of the elliptic vortex is shown in figure 2. The

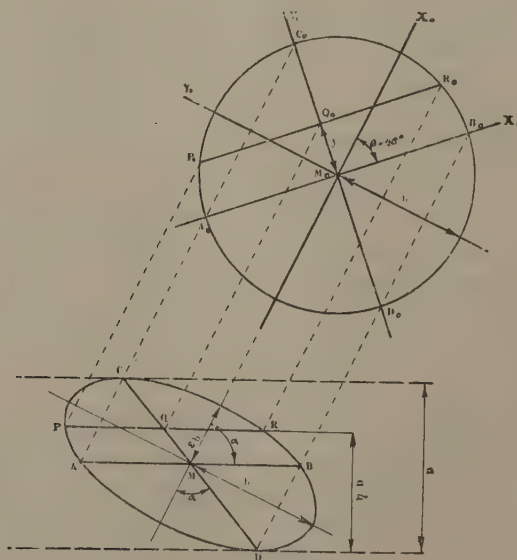


Fig. 2.

¹⁾ H. A. LORENTZ, l.c. p. 48—52.

axes of the ellipse have the lengths $2b$ and $2\epsilon b$, in which expression ϵ has the value $1/2 (\sqrt{15} - \sqrt{6}) = 0,475$; the smaller one makes the angle $\arctg \frac{1}{\epsilon} = \alpha$ with the direction of the mean motion. The conjugated diameters AB and CD correspond to the diameters of the circle $A_0 B_0$ and $C_0 D_0$, which make angles of 45° with the directions of the axes of the ellipse. Besides the system of coordinates x_0, y_0 used by LORENTZ, the system x_1, y_1 along $M_0 B_0$ and $M_0 C_0$ will be introduced.

From the formulae given by LORENTZ at page 49 we deduce the following expression for the value of uv in a point of the vortex, corresponding to the point x_0, y_0 of the circle:

$$M_0 = -uv = \frac{1}{2} (x_0^2 - \epsilon^2 y_0^2) \omega^2 \sin 2\alpha + \epsilon x_0 y_0 \omega^2 \cos 2\alpha = \left\{ \begin{aligned} &= \frac{\epsilon}{1 + \epsilon^2} \omega^2 \{ x_1^2 (1 - \epsilon^2) + x_1 y_1 (1 + \epsilon^2) \} \end{aligned} \right\} \quad (23)$$

For the determination of the mean value of uv along a line parallel to the axis of x , it is necessary to calculate the integral of M_0 along a line PR which is parallel to the same axis. This line corresponds to the line $P_0 R_0$ of the circle; the lengths of these lines are in the constant proportion:

$$\frac{AB}{A_0 B_0} = \frac{1}{\sqrt{2} \sin \alpha} = \sqrt{\frac{1 + \epsilon^2}{2}}$$

Hence this integral takes the value:

$$M_1 = \int_{-\sqrt{1 - y_1^2}}^{+\sqrt{1 - y_1^2}} dx_1 \frac{\epsilon \omega^2}{\sqrt{2} (1 + \epsilon^2)} \{ x_1^2 (1 - \epsilon^2) + x_1 y_1 (1 + \epsilon^2) \}. \quad (24)$$

As has been mentioned already above, ω is a function of $r_0 = \sqrt{x_0^2 + y_0^2} = \sqrt{x_1^2 + y_1^2}$; this function will be taken to be:

$$\omega = c (b^2 - r_0^2)^{5/4} = c (b^2 - x_1^2 - y_1^2)^{5/4} \quad (25)$$

The second term of the integral vanishes on account of the symmetry of ω ; the first term gives:

$$M_1 = \frac{\sqrt{2} \epsilon (1 - \epsilon^2)}{\sqrt{1 + \epsilon^2}} c^2 \int_0^{\sqrt{b^2 - y_1^2}} dx_1 x_1^3 (b^2 - x_1^2 - y_1^2)^{5/2}$$

¹⁾ In the formulae below everywhere c^2 occurs; the sign of c is of no importance.

or, using the substitution:

$$\begin{aligned}
 x_1 &= \sqrt{b^2 - y_1^2} \sin \chi, \\
 M_1 &= \frac{\sqrt{2\varepsilon(1-\varepsilon^2)}}{\sqrt{1+\varepsilon^2}} c^2 (b^2 - y_1^2)^4 \int_0^{\pi/2} d\chi \sin^2 \chi \cos^6 \chi = \left(\right. \\
 &= \left. \frac{5\pi}{256} \frac{\sqrt{2\varepsilon(1-\varepsilon^2)}}{\sqrt{1+\varepsilon^2}} c^2 (b^2 - y_1^2)^4 \right). \quad (26)
 \end{aligned}$$

Formula (25) was chosen with a view of obtaining this latter result for M_1 , which facilitates the further calculations. If a new variable η is introduced, determined by the formula:

$$\eta = \frac{y_1 + b}{2b}$$

(it appears from this formula that η has the value 0 on the tangent at the ellipse at the point D , and takes the value 1 on the tangent at C), then equation (26) can be written:

$$M_1 = A\eta^4(1-\eta)^4 = A\varphi(\eta) \dots \dots \dots (27)$$

Here A is a factor independent of the variable η .

If we imagine a great number of these vortices to be present, all of them having the same dimensions and lying between the same tangents parallel to the axis of x , (comp. fig. 3), the amount contributed by them to the value of uv will be proportional to the function represented by (27)¹).

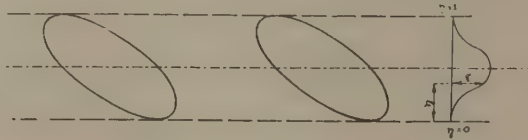


Fig. 3.

The integral of the quantity M_0 taken over the entire area of the vortex amounts to:

$$M_2 = \frac{2\pi\varepsilon^2(1-\varepsilon^2)}{63} c^2 b^9 \dots \dots \dots (28)$$

¹) Other types of motion may lead to the same form of the function determining M_1 ; for instance we may take the motion defined by the current function

$$\Psi = \eta^2(1-\eta^2)(e^{1-\eta} \cos ax - e^\eta \sin ax)$$

for values of η between 0 and 1, so that the components of the velocity have the values:

$$u = -\partial \Psi / \partial x, v = \partial \Psi / \partial y.$$

The integral of the square of the vorticity $N_z = \iint dx dy \zeta^2$ extended over the same area becomes according to the formula given by LORENTZ:

$$N_z = \frac{\pi}{4\varepsilon} (3 + 2\varepsilon^2 + 3\varepsilon^4) \int_0^b dr_0 r_0^3 \left(\frac{d\omega}{dr_0} \right)^2 = \frac{5\pi}{42} \frac{3 + 2\varepsilon^2 + 3\varepsilon^4}{\varepsilon} c^2 b^7. \quad (29)$$

From (28) and (29) we deduce:

$$\frac{N_z}{M_z} = \frac{15}{4} \frac{(3 + 2\varepsilon^2 + 3\varepsilon^4)(1 + \varepsilon^2)}{\varepsilon^3(1 - \varepsilon^2)} \frac{1}{b^2},$$

or, introducing the "thickness" D of the vortex (cf. fig. 2), so that:

$$b = D \frac{\sqrt{2(1 + \varepsilon^2)}}{4\varepsilon},$$

we get:

$$\frac{N_z}{M_z} = 30 \frac{3 + 2\varepsilon^2 + 3\varepsilon^4}{\varepsilon(1 - \varepsilon^2)} \frac{1}{D^2} = \frac{294}{D^2}. \quad (30)$$

This fraction surpasses only by a small amount its minimum value, calculated by LORENTZ:

$$14,68 \frac{2(3 + 2\varepsilon^2 + 3\varepsilon^4)}{\varepsilon(1 - \varepsilon^2)} \frac{1}{D^2} = \frac{288}{D^2} {}^1)$$

§ 5. *Distribution of the vortices over the fluid.*

It has already been remarked in § 1 and 3 that our object in this paragraph is not to analyse the true distribution of the vorticity of the fluid, but that we will construct an ideal case only, a "model", which affords us an admissible image of the behaviour of the quantities \overline{uv} and $\overline{\zeta^2}$. This model is obtained by distributing a number of elliptic vortices, of the type studied in the foregoing paragraph, over the mean current $U(y)$. In doing this we do not want to pay any attention to the abscissae of the centra of the vortices, if only their mean distribution along lines parallel to the axis of x be uniform. Positively and negatively rotating vortices are distributed uniformly through each other. If two or more vortices may happen to overlap, they may as well strengthen as enfeeble their respective fields; hence in calculating the mean values \overline{uv} and $\overline{\zeta^2}$ it is unnecessary to take account of these overlappings, and the contributions of the different vortices may be simply summed.

If for a moment we direct our attention to a special class of

¹⁾ Comp. a remark made by LORENTZ, l.c. p. 54/55. The function defined by eq. (25) above fulfils the condition: $d\omega/ds = 0$ for $s = 1$ ($s = r_0/b$).

vortices, the thickness D of which lies between the limits D and $D + dD$, and the lower tangents of which (i.e. the tangent at the point D in fig. 2) are enclosed between the limits $y = \xi$ and $y = \xi + d\xi$, then we may say that all of them are lying between the same lines parallel to the axis of x , and by what has been remarked above all of them will give proportional contributions to the field of \overline{uv} -values. As the integral $-\int dx uv$ extended over a section PR of a single vortex has been calculated in (26) and (27), we may write the contribution of the whole class:

$$b(D, \xi) \eta^4 (1 - \eta)^4 dD d\xi = b\varphi(\eta) dD d\xi$$

In this expression: $\eta = (y - \xi)/D$, and the factor $b(D, \xi) dD d\xi$ represents the product of the number of these vortices contained in a strip of unit length parallel to the axis of x , their mean intensity (i.e. the mean of c^2), and the other factors which are contained in the letter A of formula (27). If the function $b(D, \xi)$ is given, the distribution of \overline{uv} can be calculated.

It is not necessary to know the value of the quantity $\overline{\zeta^2}$ at every point of the current, its integral only over the whole breadth being wanted, which integral can be found as the sum of the integrals of ζ^2 over all vortices contained in a strip of the full breadth, and of unit length. With the aid of formula (30) we find as the contribution of the considered class of vortices:

$$\left. \begin{aligned} \iint dx dy \zeta^2 &= -\frac{294}{D^3} \iint dx dy uv = \\ &= \frac{294}{D^3} b dD d\xi \int_{\xi}^{\xi+D} dy \varphi\left(\frac{y-\xi}{D}\right) = \frac{294 b dD d\xi}{630 D} \end{aligned} \right\} \dots \dots (31)$$

A simplification further arises from the fact that the second and third equations (16) which determine τ and κ are homogeneous as regards to the intensity of the vortices. In using these equations it is allowed to multiply b with an arbitrary factor. The true value of σ is found from the principal equation (17). It would be possible to calculate the true value of b afterwards, but this is of no use.

The problem put in paragraph 3: to make σ as great as possible, obliges us to search for a function $b(D, \xi)$ which gives a value of $-\overline{uv}$ as nearly constant as possible. Two rather simple types of functions will be discussed.

I. We will begin with an investigation of what can be reached if all vortices have the same thickness D . In that case in order to

obtain a constant value of $-\overline{uv}$, it is necessary to make b independent of ξ , in other words to distribute the vortices uniformly over the breadth of the current. However, it is obvious that the vortices cannot pass through the walls of the channel; hence we must take:

$$\left. \begin{aligned} b &= \text{constants, if } 0 < \xi < 1 - D \\ b &= 0, \text{ if } \xi < 0 \text{ or } \xi > 1 - D \end{aligned} \right\} \quad (32)$$

Consequently the quantity $-\overline{uv}$ will have a constant value in the region defined by: $D < y < 1 - D$ only; in the two remaining strips it decreases to zero.

With the omission of a constant factor, the following expressions for $-\overline{uv}$ are found:

a) if $y < D$:

$$\begin{aligned} -\overline{uv} &= \int_0^y d\xi \varphi\left(\frac{y-\xi}{D}\right) = D \int_0^{y/D} d\eta \varphi(\eta) = \\ &= \frac{D}{630} \left\{ 126\left(\frac{y}{D}\right)^4 - 420\left(\frac{y}{D}\right)^5 + 540\left(\frac{y}{D}\right)^6 - 315\left(\frac{y}{D}\right)^7 + 70\left(\frac{y}{D}\right)^8 \right\} \end{aligned} \quad (33)$$

b) if $D < y < 1 - D$:

$$-\overline{uv} = \int_{y-D}^y d\xi \varphi\left(\frac{y-\xi}{D}\right) = D \int_0^1 d\eta \varphi(\eta) = \frac{D}{630}$$

c) if $y > 1 - D$: in the expression given under a) y has to be replaced by $1 - y$.

By means of these formulae we find:

$$\begin{aligned} -\int_0^1 dy \overline{uv} &= \frac{D}{630} (1 - D) \\ \int_0^1 dy (\overline{uv})^2 &= \left(\frac{D}{630}\right)^2 (1 - 1,172 D). \end{aligned}$$

hence:

$$\tau = 0,828 D + \dots \quad (34)$$

All vortices being of the same dimensions, equation (30) gives immediately:

$$\alpha = \frac{294}{D^2} \dots \quad (35)$$

Inserting these values into equation (17):

$$\sigma = \frac{1}{0,828 DR} - \frac{294}{0,828 D^2 R^2} - \dots \quad (36)$$

(if the terms of the highest order only are written down). This formula gives a maximum value for σ if the thickness D of the vortices is determined by:

$$D = \frac{29,7}{\sqrt{R}} \quad (37)$$

which gives:

$$\sigma = \frac{0,027}{\sqrt{R}} \quad (38)$$

The coefficient C of the resistance formula (1) now becomes, according to (18):

$$C = \frac{S}{\rho V^2} = \frac{0,027}{\sqrt{R}} + \text{terms of the order } \frac{1}{R} \quad (39)$$

C diminishes proportionally to $\frac{1}{\sqrt{R}}$; hence we do not obtain the quadratic law of resistance, but the resistance appears to be proportional to the $1\frac{1}{2}$ -power of the velocity. This does not conform to the result of paragraph 3. In the latter paragraph, however, it was assumed that the most intensive vorticity was concentrated in the neighbourhood of the walls only, whereas in the model considered above it is distributed uniformly over the whole breadth. If all vortices have the same dimensions, it is not possible to distribute them otherwise, without disturbing the field of uv -values. Hence we must try to obtain a better result by using vortices of different dimensions.

II. If we take vortices of different dimensions, say with thicknesses ranging from $D=1$ to a lower limit D_0 (to be determined later on), the thickness of the boundary layers in the most favourable case will be of the same order of magnitude as D_0 . The same applies to the quantity τ . If now the contribution of the vortices of thickness D to the integral $\int \xi^2 dy$ becomes asymptotically proportional to $\frac{dD}{D^2}$ for small values of D , the value of this integral will become of the order of magnitude of $\frac{1}{D_0}$. In this case we shall be in the circumstances considered in the deduction of equations (19) and (20). Paying attention to equation (31), it is necessary that $B = \int b d\xi$ shall be proportional to $\frac{1}{D}$ for small values of D .

Now it appears that a distribution of vortices fulfilling these

conditions can be found, if all vortices are put against the walls. If this be done, it is of course unnecessary to use the variable ξ introduced in the beginning of this paragraph, as the positions of all vortices are fixed. Only a determination of the function $B(D)$ is wanted. The following form of this function gives the right distribution of \overline{uv} -values:

1. the class of vortices whose thicknesses lie between the limits D and $D+dD$ have a total intensity proportional to $B dD = 2 \frac{dD}{D}$; these vortices are divided into two equal groups, each of them situated along one of the walls;

2. besides the vortices mentioned under 1), there is a number of vortices of thickness $D=1$, which have the total intensity $1/4$ (in same unit as used above).

With this determination of $B(D)$, the value of $-\overline{uv}$ appears to be, if $D_0 < y < 1-D_0$:

$$\begin{aligned} -\overline{uv} &= \int_y^{1-D_0} \frac{dD}{D} \varphi\left(\frac{y}{D}\right) + \int_{1-y}^1 \frac{dD}{D} \varphi\left(\frac{1-y}{D}\right) + \frac{1}{4} \varphi(y) = \\ &= \int_y^1 \frac{d\eta}{\eta} \varphi(\eta) + \int_{1-y}^1 \frac{d\eta}{\eta} \varphi(\eta) + \frac{1}{4} \varphi(y) = \\ &= \frac{1}{280} \end{aligned} \quad (40)$$

The first term represents the contribution of the vortices lying along the wall $y=0$; of these vortices only those are of importance for which $D > y$. The second term represents the contribution of the vortices situated at the other side; here only those for which $D > 1-y$ are of importance. The third term represents the contribution of the group of vortices whose thickness D is equal to 1¹⁾.

¹⁾ If we should take the quantity B proportional to D^{-n} , with $n < 1$, the integral $\int \xi^2 dy$ would take a smaller value, but now the first term of equation (40) which gives the contribution of the vortices situated against the wall $y=0$, would become:

$$\int_y^1 \frac{dD}{D^n} \varphi\left(\frac{y}{D}\right) = y^{1-n} \int_y^1 d\eta \eta^{2+n} (1-\eta)^4 \quad (\text{for } y > D_0)$$

If y becomes small, this expression approaches to zero. Only if $n=1$ it approaches to a value independent of y , which is necessary in order that a constant value of $-\overline{uv}$ at all points outside of the boundary layer may be obtained.

In the boundary layer defined by $0 < y < D_0$, the value of $-\overline{uv}$ is found to be:

$$\left. \begin{aligned} -\overline{uv} &= \int_{D_0}^1 \frac{dD}{D} \varphi\left(\frac{y}{D}\right) + \int_{1-y}^1 \frac{dD}{D} \varphi\left(\frac{1-y}{D}\right) + \frac{1}{4} \varphi(y) = \\ &= \frac{1}{280} - \int_y^{D_0} \frac{dD}{D} \varphi\left(\frac{y}{D}\right) = \\ &= \frac{1}{280} \left\{ 70 \left(\frac{y}{D_0}\right)^4 - 224 \left(\frac{y}{D_0}\right)^5 + 280 \left(\frac{y}{D_0}\right)^6 - 160 \left(\frac{y}{D_0}\right)^7 + 35 \left(\frac{y}{D_0}\right)^8 \right\} \end{aligned} \right\} \quad (41)$$

Using the formulae (40) and (41) we find:

$$\begin{aligned} - \int_0^1 dy \overline{uv} &= \frac{1}{280} (1 - 0,889 D_0) \\ \int_0^1 dy (\overline{uv})^2 &= \left(\frac{1}{280}\right)^2 (1 - 1,068 D_0) \end{aligned}$$

and by means of the latter there results:

$$\tau = 0,710 D_0 - \dots \dots \dots (42)$$

The value of α can be calculated in the following way: The vortices having thicknesses between the limits D and $D + dD$ contribute to the integral $-\int dy \overline{uv}$ the amount:

$$2 \frac{dD}{D} \int_0^D dy \varphi\left(\frac{y}{D}\right) = \frac{dD}{315};$$

hence, according to (30), to the integral $\int dy \overline{\xi^2}$:

$$\frac{294}{315} \frac{dD}{D}$$

To this must be added the contribution of the vortices with thickness 1, amounting to:

$$\text{in } - \int dy \overline{uv} : \frac{1}{2520};$$

$$\text{hence in } \int dy \overline{\xi^2} : \frac{294}{2520}.$$

Adding all parts together, we get:

$$\int dy \overline{\xi^2} = \frac{294}{315} \left(\frac{1}{D_0} - 1 \right) + \frac{294}{2520} = \frac{294}{315} \left(\frac{1}{D_0} - \frac{7}{8} \right).$$

Finally the value of α becomes:

$$\alpha = \frac{261}{D_0} + \dots \quad (43)$$

The values given by (42) and (43) are inserted into the principal equation (17); retaining the terms of the highest order only, we find:

$$\sigma = \frac{1}{0,710 D_0 R} - \frac{261}{0,710 D_0^2 R^2} - \dots \quad (44)$$

σ attains its maximum value if the lower limit D_0 of the thickness of the vortices is determined by:

$$D_0 = \frac{522}{R} \quad (45)$$

This is much below the value of D given by equation (37). Using (45) we find:

$$\sigma = 0,00135 + \dots \quad (46)$$

and the coefficient of the resistance formula becomes:

$$C = \frac{S}{\rho V^2} = 0,00135 + \text{terms of the order } \frac{1}{R} \quad (47)$$

So this arrangement of the vortices leads to the *quadratic* law of resistance.

§ 6. Discussion.

In paragraph 5 II we have found the value 0,00135, as a higher limit of the coefficient C of the resistance formula using an idealized model of the distribution of the vorticity in a turbulent current.

If it is possible to calculate C without the use of this special model, using equations (17) and (18) and conditions (6) and (7) only, a still higher limit will probably be found. At the other side if we compare the value of C obtained here to the value given by formula (4b), it appears that in the region which is of importance: $R = 10000$ to 1000000 , the value of C is *too high*.¹⁾

Hence we may assert that the true resistance is not the highest possible resistance. In order to determine the true state of affairs, a further condition will be necessary.

From the result that the value of C appears to be *too high*, we may deduce that the distribution of the value of $-\overline{uv}$ over the current is too uniform. Paying attention to the results of measurements of the distribution of the velocity over the breadth of the

¹⁾ According to COUETTE's experiments turbulence sets in at $R = \text{ca. } 1900$.

current, we may expect that $-\overline{uv}$ has not a constant value between the boundary layers, but that it is slightly "rounded off". This might be ascribed to slight irregular displacements of the vortices caused by the irregularly distributed velocities which they impart to each other. This "Brownian" movement might give a distribution of the smaller vortices resembling the one determined by the law of BOLTZMANN-MAXWELL for a gas under the influence of gravity, which possibility has been pointed out by VON KÁRMÁN in the lecture mentioned above.

The true distribution of vorticity in the turbulent motion will take some mean position between the two extremes of paragraph 5 (uniform distribution over the whole breadth with C proportional to

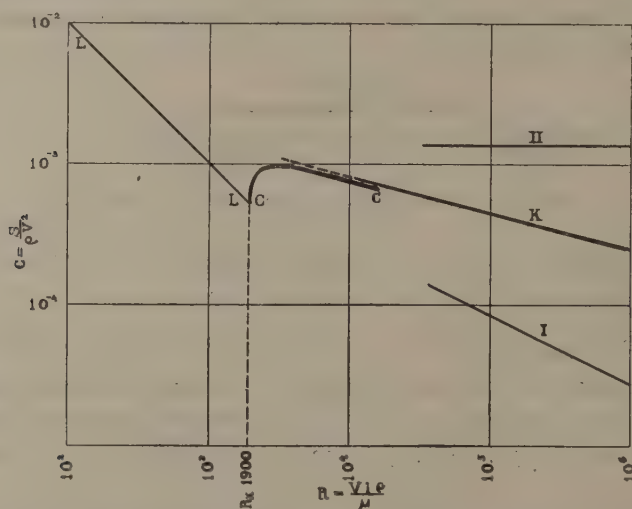


Fig. 4. Logarithmic-scale diagram of the dependence of C on R .

Curve L : laminar region, $C = \frac{1}{R}$ (form. 3).

Curve C : results of COUETTE's experiments (the value of R has been calculated using $\mu = 0,01096$, comp. COUETTE, l. c. p. 460).

Curve K : $C = 0,008 R^{-1/4}$ (form. 4b), deduced from the investigations by VON KÁRMÁN on the behaviour of $U(y)$.

Curve I : formula (39), deduced from the supposition that all vortices have the same dimensions, and are uniformly distributed over the section.

Curve II : formula (47), deduced from the supposition that the vortices have different dimensions, and are lying against the walls.

$\frac{1}{\sqrt{R}}$, or the best ordered arrangement with all vortices along the walls and C equal to a (high) constant value).

For the sake of comparison the formulae (39), (47) and (4b) have been represented together in fig. 4 at a logarithmic scale.

§ 7. *Motion of a fluid between two fixed parallel walls.*

The motion of a fluid between two fixed parallel walls may be treated according to the same scheme as has been used for the motion between a fixed and a moving wall. As the former case has somewhat more resemblance to the types of motion occurring usually in practical cases, the principal features of the calculation will be mentioned here.

The distance of the walls will be taken equal to h ; the mean velocity of the current is denoted by V ; the pressure gradient $-dp/dx$ will be denoted by J . — REYNOLDS' characteristic number becomes: $R = Vh\rho/\mu$; the coefficient of the resistance formula is written $C = Jh/\rho V^2$. Equation (8) of paragraph 2 has to be replaced by the following equation governing the principal motion:

$$\mu \frac{d^2 U}{dy^2} - \frac{d}{dy} (\rho \overline{uv}) = -J \quad \dots \quad (48)$$

A first integration of this formula gives:

$$\mu \frac{dU}{dy} - \rho \overline{uv} = J \left(\frac{h}{2} - y \right) \quad \dots \quad (49)$$

The constant of the integration is determined by observing that on account of the symmetry of the arrangement both quantities dU/dy and \overline{uv} vanish for $y = h/2$. On integrating a second and a third time, and observing that $U = 0$ at both walls, we get:

$$\mu V h = \frac{1}{12} J h^3 - \int_0^h dy \rho y \overline{uv} \quad \dots \quad (50)$$

This equation replaces formula (11). Condition (9) which expresses the dependance of the relative motion on the principal motion, retains its form. Now firstly, using (49), we eliminate dU/dy from (9); then using (50), we eliminate J and we obtain:

$$\frac{\mu V}{h} = \frac{\frac{1}{12} \int_0^h dy \{ \rho^2 (\overline{uv})^2 + \mu^2 \overline{S}^2 \} - \frac{1}{h^2} \left(\int_0^h dy \rho y \overline{uv} \right)^2}{\frac{1}{h} \int_0^h dy \rho y \overline{uv}} \quad \dots \quad (51)$$

After the introduction of undimensioned variables, we make use of the abbreviations:

$$\left. \begin{aligned} \int_0^1 dy \, y \, \overline{uv} &= \sigma \\ \frac{1}{12} \int_0^1 dy \, (\overline{uv})^2 &= (1+\tau) \sigma^2 \\ \frac{1}{12} \int_0^1 dy \, \overline{\xi^2} &= \kappa \sigma \end{aligned} \right\} \dots \dots \dots (52)$$

The equations (50) and (51) now reduce to:

$$\sigma\tau + \frac{\kappa}{R^2} = \frac{1}{R} \dots \dots \dots (53)$$

$$\frac{1}{12} \frac{Jh}{\rho V^2} = \frac{C}{12} = \sigma + \frac{1}{R} \dots \dots \dots (54)$$

Distribution of the vortices over the fluid.

As appears from equation (49) the value of $\mu \frac{dU}{dy}$ will be small compared to that of $J\left(\frac{h}{2} - y\right)$ (as is the case for the real motion) only if $-\rho \overline{uv}$ becomes approximately equal to $J\left(\frac{h}{2} - y\right)$. Or, using the undimensioned variables introduced above, we may say that $-\overline{uv}$ ought to be proportional to $\frac{1}{2} - y$.

Hence the quantity \overline{uv} must take a negative value in the neighbourhood of the wall $y=0$, and it must take a positive value at the other wall. This can be obtained if we use two groups of vortices whose positions are symmetrical with respect to each other. In the first place a group of elliptic vortices having the same position as those described in paragraphs 4 and 5 (i.e. with the long axis extended from the second to the fourth quadrant) is put in against the wall $y=0$. The contribution of these vortices to the field of values of \overline{uv} will be denoted by

$$-(\overline{uv})_I = \psi(y).$$

Then a second group is put in, situated symmetrically against the other wall: the contribution of the latter to \overline{uv} will be:

$$-(\overline{uv})_{II} = \psi(1-y).$$

The contributions of both groups to the integral $\int dy \bar{\zeta}^2$ are of course equal and of equal signs.

If we now take vortices having thicknesses ranging from 1 to a minimum value D_0 , and we take their intensities proportional to:

$$B dD = \left(\frac{1}{D} - \frac{3}{4} \right) dD \quad \dots \quad (55)$$

(this expression has a positive value for all values of D), then we obtain for values of y lying between D_0 and $1 - D_0$ the following expression of $\psi(y)$ (with the omission of a constant factor):

$$\begin{aligned} \psi(y) - \int_y^1 dD \left(\frac{1}{D} - \frac{3}{4} \right) \varphi \left(\frac{y}{D} \right) = \\ = \frac{1}{140} \left\{ \frac{1}{2} - y + 7y^2 - 14y^3 + 10y^4 - \frac{5}{2}y^5 \right\} \end{aligned}$$

from which follows:

$$\psi(y) - \psi(1-y) = \frac{1}{140} \left(\frac{1}{2} - y \right) \quad \dots \quad (56)$$

Hence between the boundary layers the values of \overline{uv} are correctly distributed.

Within each boundary layer $|\overline{uv}|$ decreases from $1/280$ to zero. The full expression of the value of \overline{uv} having been worked out, we obtain the integrals:

$$\begin{aligned} \int_0^1 dy y \overline{uv} &= \frac{1}{1680} (1 - 2,667 D_0 + \dots) \\ \frac{1}{12} \int_0^1 dy (\overline{uv})^2 &= \left(\frac{1}{1680} \right)^2 (1 - 3,204 D_0 + \dots) \end{aligned}$$

from which:

$$\tau = 2,129 D_0 - \text{terms of the order } D_0^2 \dots \quad (57)$$

The value of the integral $\int_0^1 dy \bar{\zeta}^2$ becomes:

$$2 \int_{D_0}^1 dD \frac{294}{630} \frac{1}{D} \left(\frac{1}{D} - \frac{3}{4} \right) = \frac{294}{315} \left(\frac{1}{D_0} - \frac{3}{4} \lg \frac{1}{D_0} - \dots \right).$$

This gives:

$$\alpha = \frac{131}{D_0} \left(1 - \frac{3D_0}{4} \lg \frac{1}{D_0} + \text{terms of the order } D_0 \dots \right). \quad (58)$$

The results of (57) and (58) are substituted into equation (53), and the maximum value of σ is determined. This maximum occurs if:

$$D_0 = \frac{262}{R} \left(1 - \frac{98}{R} \lg \frac{R}{262} \dots \right)$$

Finally equation (54) gives:

$$C = 0,0108 + \frac{2,11}{R} \lg R + \text{terms of the order } \frac{1}{R} \quad (59)$$

Discussion.

In this case too the *quadratic* law of resistance is asymptotically arrived at (for values of R surpassing 100000 the logarithmic term is little more than 2% of the constant term). Just like what occurred in the more simple case the value of the coefficient C is *too high*. For channels with smooth walls von MISES gives that C ranges from 0,006 to 0,0024 if R ranges from 10000 to the greatest values obtained; the formula derived by von KÁRMÁN's theory gives:

$$C = \text{ca. } 0,07 R^{-1/4}$$

For channels with rough walls the dependance of the coefficient C on the value of R is usually very small, so that a quadratic resistance formula can be used, the value of C depending, however, on the dimensions of the irregularities of the walls as compared to the diameter of the channel. The value of C is much higher than in the case of smooth walls; it may even surpass that given by (59). So GIBSON mentions values ranging to 0,015 for old cast iron tubes or channels, lightly tuberculated¹⁾.

*Laboratorium voor Aero- en Hydrodynamica der T. H.
Delft, May 1923.*

¹⁾ The constant term of C in this formula has a value of 8 times that of formula (47). An elementary but superficial comparison of the magnitude of the frictional forces exerted on the walls in both cases leads to the same result.

²⁾ R. VON MISES, l.c. p. 63, in connection with the definition of r , given at p. 83/84. In the case of a channel of infinite depth as the one treated here, r is equal to h .

A. H. GIBSON, *Hydraulics and its applications* (1919), p. 209 (in the formula mentioned at p. 206 is m is $\frac{1}{2}$ time the quantity r introduced by VON MISES; comp. GIBSON, l.c. p. 194).

Comp. also L. SCHILLER, *ZS. für angew. Math. u. Mechanik*, **3**, p. 2, 1923. and others.

Paléontologie. — „*Sur quelques nouveaux insectes des lignites oligocènes (Aquitanien) de Rott, Siebengebirge (Rhénanie).*
Par FERNAND MEUNIER.

(Présenté par Mr. le Prof. K. MARTIN dans la séance du 29 septembre 1923).

Cette contribution à la faune de Rott, fait suite à des travaux antérieurs, commencés en 1894 et dont la bibliographie complète est donnée ici.

Ces nouvelles espèces ont été rencontrées dans les gisements rhénans par M. H. BAUCKHORN. Il s'agit d'abord d'un coléoptère qui semble voisin de *Otiorhynchus induratus* Heyd. mais dont les yeux, au lieu d'être allongés, sont arrondis et de *Varus ignotus* Schlechtendal (*Brachymycterus curculionoides* Heyd.) Il paraît avoir des traits de ressemblance avec *Phytonomus firmus* Heer des couches sannoisiennes de Provence (France). Si la morphologie de la forme de Rott était moins frustement indiquée, on pourrait la comparer avec *Laccopygus nilesii* Scudder du miocène de Florissant (Etats-Unis), avec *Geralophus saxonus* Scudd. qui présente une striation très voisine. Par la présence des articles des antennes (le 1^{er} article est malheureusement altéré par la fossilisation), je range ce nouveau fossile de Rott dans le genre *Laccopygus* Scudder. De nouveaux documents s'imposent avant de préciser les diagnoses de *Otiorhynchus induratus* Heyd. *Brachymycterus curculionoides* Heyd. et de *Varus ignotus* Schlechtendal. Tout porte à croire que la nouvelle espèce rhénane, à antennes si curieuses, est à maintenir dans le genre *Laccopygus* Scudd. Disons encore, que d'autres espèces de Rott, établies par v. Heyden, devraient être redécrites d'après des fossiles en meilleur état de conservation. Il y aurait aussi lieu de donner de nouveaux dessins au trait des principaux organes de ces coléoptères.

Cette note contient aussi de courtes remarques, relatives à deux hyménoptères terebrantia. Un très minuscule, mais très gracieux Proctotrypide, *Archaeobelyta superba* Meun. ♂. La ♀ a été décrite dans *Miscellanea entomologica* (t. XXVI, p. 82 pl. 1 fig. 3, 1922) Dans la famille des Ichneumonidae, du groupe des Pimplinae, il est question d'une nouvelle espèce de *Pimpla*. Parmi les diptères, mentionnons encore la présence d'un Tipulidae *Polyneura*, se plaçant avec certitude dans le genre *Limnophila* Maquart. Cette notice

contient encore des remarques et des reproductions phototypiques ¹⁾ de plusieurs espèces intéressantes notamment d'un coléoptère Nitidulidae du genre Nitidula Fabr. ensuite, un hyménoptère Chalostagastra ou Tenthredinidae se groupant parmi les vrais Tenthredo. Dans le monde des Aculéates, il a été observé un Formicidae, de grande taille, se rangeant parmi des Ponera Latr. (*P. elegantissima* Meunier). Il est aussi signalé un petit diptère, qui appartient vraisemblablement au genre Phora Linné. M. BAUCKHORN a aussi trouvé à Rott un Tipulidae du genre Erioptera Meig. (*E. oligocaenica* Meun.).

DESCRIPTION DES ESPÈCES ¹⁾

I. Coleoptera.

I. Curculionidae.

Genre *Laccopygus* Scudd.

Laccopygus rhenanus Meun.

Long. du corps 5 mm., larg. 3 mm. Par la morphologie du corps, cette espèce est voisine de *L. nilsii* Scudd. du miocène de Florissant (Etats-Unis). Tête robuste, rostre court, yeux paraissant arrondis; antennes composées de 7 articles plus longs que larges (cylindriques) et terminés par un bouton apical, paraissant formé de 3 divisions; le bouton apical est ovoïde, très distinct.

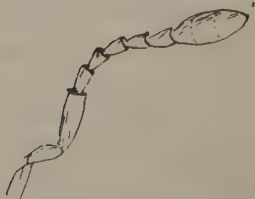


Fig. 1. Antenne de *Laccopygus rhenanus*.

Thorax plus large que long la fossilisation empêche de décider s'il était ponctué ou orné d'une ponctuation rugueuse. Elytres, recouvrant entièrement les segments de l'abdomen qui sont très distincts. Pattes robustes.

II. Nitidulidae.

Genre *Nitidula* Fabre.

Aucun coléoptère de cette famille n'a encore été rencontré sur les feuillettes de Rott. On a signalé quelques formes des couches d'Oeningen et de RADOBOY et S. H. SCUDDER a décrit *Nitidula* prior des couches miocéniques de Florissant.

Nitidula robusta n.sp.

Long. du corps 6 mm., largeur 2 mm.

L'insecte trouvé à Rott, est malheureusement couché sur le dos, ce qui empêche d'étudier les caractères des élytres et le dessus du thorax. Corps ovale, trapu. Tête robuste, un peu proéminente vers

¹⁾ A cause des frais considérables d'impression, les planches qui accompagnent ce travail n'ont pu être données actuellement.

le clypeus. Antennes atteignant la moitié de la longueur du thorax et paraissant être composées de 11 articles, courts et saillants, dont les 2 ou 3 derniers constituent une sorte de bouton apical. Thorax sinueux, à la partie antérieure, arrondi aux angles antérieurs; il est trapézoïdiforme, bien développé. Les segments de l'abdomen, très distincts, arqués; le dernier segment ou pygidium acuminié. Pattes très robustes, fémurs bien développés; la fossilisation ne permet pas de décrire la morphologie des articles tarsaux. Disons encore que chez cette espèce les articles des antennes sont plus larges que longs et serrés les uns contre les autres. (Chez le seul specimen observé de Rott). L'espèce de Florissant, *Nitidula prior* Scudd. a plusieurs traits de ressemblance avec celle trouvée par M. BAUCKHORN sur les schistes rhénans. Le genre *Saronia* a de l'affinité, on le sait, avec le genre *Nitidula* Fabr. De nouveaux documents d'études s'imposent avant de donner la diagnose complète de cette espèce.

II. *Hymenoptera*.

Terebrantia.

Chalastogastra ou *Tenthredinidae*.

Des couches de Rott, on connaît 2 mouches à scie de cette famille: *Pinicolites graciosus* Meun. et *Tenthredo fasciata* Meun. Des plaquettes d'Aix, en Provence, j'ai décrit *Hylotomites robusta* Meun. D'autres *Chalastogastra* ont été signalés des couches tertiaires de Florissant par T. D. A. COCKERELL. Citons notamment *Tenthredella oblita*, *Palaeotaxonus vetus* et *Eriocampoides minus*.¹⁾

Genre *Tenthredo* Linné.

Tenthredo fasciata n.sp.

A Rott, on a observé un *Chalastogastra* qui se reconnaît, a première vue, par la présence de bandes transversales ornant la partie postérieure des segments de l'abdomen; ce dernier organe longuement ovoïde. Les parties médiane et latérale du thorax garnies de bandes longitudinales. Tarière bien développée et offrant la morphologie générale des espèces du genre *Tenthredo* Linné. Pattes robustes. Deux cellules radiales aux ailes antérieures et 4 cellules cubitales, dont la 2^{ième} et la 3^{ième} reçoivent chacune une nervure recurren-te. Cellule anale des ailes postérieures non appendiculée; à cette dernière paire d'ailes, il y a 2 cellules discoïdales fermées. La tête de cette espèce n'est malheureusement pas conservée sur le schiste. La longueur du corps (présumée) de cet hyménoptère, y compris la tête, devait être environ de 13 millimètres.

¹⁾ Proc. U. S. Nat. Mus. vol. 53, pp. 389—390 Washington 1917.

Empreinte et contre empreinte. Coll. H. BAUCKHORN de Siegburg.
 Observation: Chez les *Perineura* HARTIG, la cellule anale des ailes postérieures est appendiculée.

Proctotrypidae.

Archaeobelyta superba MEUNIER.

(Miscellanea Entomologica t. XXV p. 84 pl. 1 fig. 3, Toulouse 1922).

Ce sexe est plus grêle et plus élancé que la ♀. Les antennes ont des articles de moindre diamètre ce qui donne à leur morphologie générale un aspect plus régulier, de plus, l'extrémité des antennes n'est guère épaissie (chez la ♀, le bout antennaire l'est distinctement). La veination des ailes est pareille à celle de la ♀; les pattes, un peu moins robustes, ne présentent aucun caractère particulier.

Coll. BAUCKHORN, Siegburg.

Observation: C'est la première fois qu'un hyménoptère, de si petite taille, a été trouvé sur les schistes européens. En son intéressant mémoire, "The parasitic Hymenoptera of the tertiary of Florissant (Colorado) Cambridge 1910", CHARLES BRUES a figuré et donné les diagnoses d'espèces dont la préservation est loin d'être aussi complète que *Archaeobelyta superba* Meun. ♂ et ♀. Pour finir, disons encore que l'ambre de la Baltique et le copal de diverses provenances africaines, sont riches en inclusions de *Proctotrypidae*. Cette étude à peine esquissée, par MENGE attend encore la venue d'un monographe. Autrefois (Ann. de la Soc. scient. de Bruxelles 1901), j'ai signalé la riche faunule que contient l'ambre et le copal en fait de *Mymaridae* ou „atomes ailés”.

Ichneumonidae.

Pimplinae.

On a rarement signalé des *Pimplinae* des couches fossiles de Rott, toutefois Osw. Heer a décrit un *Acoenites* des feuilletts de Rado-boy et Brues les a signalés du miocène de Florissant. Je viens de donner la description d'une nouvelle espèce de l'Aquitaniien de Rott „*Acoenites Statzi*” (Miscellanea Entomologica t. XXVI, p. 85 pl. 1 fig. 4. Toulouse 1922 (23). M. Bauckhorn m'a communiqué un *Pimplinae* dont malheureusement la tête, le thorax, l'abdomen et les pattes sont trop frustement indiqués pour en donner une minutieuse diagnose, et établir les rapports probables de ce fossile aquitaniien avec les *Ephialtes* Gravenhorst. Toutefois, la conservation des deux paires d'ailes est si parfaite, qu'il y a lieu, dès à présent de le nommer. Je propose de l'appeler *Pimpla Morleyi* en honneur du distingué

Ichneumonologue M. MORLEY du Musée de Suffolk, (Angleterre). Chez ce *Pimpla*, la cellule aréolaire au lieu d'être triangulaire et pétiolée comme c'est souvent le cas chez diverses espèces de *Pimpla*, n'est pas entièrement pentagonale comme on le remarque chez les espèces du sous-genre *Delomerista* Foerster. De plus, la 5ième nervure des ailes antérieures (nervus basalis) se raccorde entièrement avec la 6ième nervure ou nervulus de manière à produire une ligne concave. Longueur du corps 5mm.? Longueur de l'aile antérieure 5mm. Largeur de l'aile antérieure $2\frac{1}{2}$ mm.

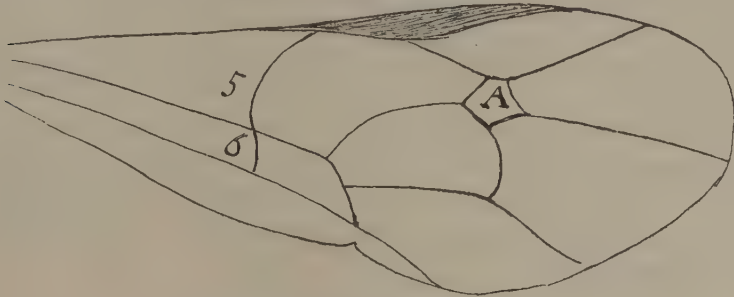


Fig. 2. Aile de *Pimpla Morleyi* n. sp.

Aculeata.
Formicidae.

VON HEYDEN a signalé à Rott la présence du genre *Formica*. Naguère, j'ai donné les diagnoses des espèces se classant dans les genres *Myrmica*, *Tapinoma* et *Formica*. La nouvelle espèce, décrite ici, diffère à première vue, par la taille de *Ponera rhenana*.

Ponera elegantissima n. sp.

Cette espèce se sépare des formes suivantes mentionnées par Osw. HEER: *Ponera fuliginosa*, *oeningensis* et *radoboyana*, *P. affinis* *P. croatica*, *P. longaeva*, *P. nitida*, *P. grassinervis*, *P. elongatula*, *P. ventrosa* et *P. globosa*. Par la veination des ailes, elle est voisine de *Ponera fuliginosa* et *oeningensis*, par sa grande taille, elle se sépare immédiatement de *Ponera rhenana* Meun. des couches aquitaniennes de Rott.

Tête robuste ovale mandibulus trapues, paraissant arrondies à leur extrémité. Pétiole de l'abdomen très appréciable. Abdomen formé de 4 segments et nettement ovoïde. Ailes antérieures à nervure transverso-radiale en connection directe avec la cellule limitant la 2ième cellule cubitale. Chez *P. rhenana*, ces 2 transversales sont assez éloignées l'une de l'autre¹⁾.

¹⁾ MEUNIER, F., Verhandeligen der K. Akademie van Wetenschappen, tweede Sectie, Deel XX, N. 1, fig. 6, Amsterdam 1917.

*Diptera.**Tipulidae.**Eriopterinae.*

Les Tipulidae, si fréquents sur les schistes miocéniques de Florissant, sont rares sur les couches des lignites des Sept-Monts (Rhénanie). On sait que l'ambre contient une curieuse faunule de ces intéressants diptères¹⁾. En 1917²⁾, j'ai signalé une aile de vrai Tipula de ce gisement oligocène et fait de courtes remarques relatives aux espèces décrites naguère par v. HEYDEN. Les diptères de ce groupe n'ont pas encore été signalé dans le copal subfossile de Zanzibar. Les couches d'Aix en Provence (France) ont fournies quelques beaux spécimens de Tipularinae³⁾.

On connaît actuellement 4 espèces de Tipulidae des schistes tertiaires du Rhin: Cladoneura robusta Meun. Cyttaromyella bastini Meun. et l'espèce décrite ci-dessous. Il faut encore y ajouter une nouvelle espèce de Limnophila Macq, admirable de conservation, dont la diagnose suit.

Erioptera oligocaenica n. sp.

Tête globulaire, robuste. Antennes à articles de la base de plus fort diamètre que ceux de l'extrémité. Abdomen allongé. Ailes plus longues que le corps; nervure transversale radiale (R) et radio-médial bien distincte. La transversale médio-cubitale part de M_1 et non de la médiane. Secteur du radius (préfourche d'après Osten-Sacken) nettement concave, ce secteur comprend 5 nervures ($R_1 + R_5$). La médiane est longement fourchue ($M_1 + M_2$). Le cubitus (Cu) est simple, il en est de même de la première et de la 2ième nervure anale. Pas de cellule discoidale.

Longueur du corps: 5 mm. longueur de l'aile 6 mm.

Observation: Par sa forme concave, le secteur du radius rappelle celui des Tipulidae Limnophilinae.

*Limnophilinae.**Genre Limnophila Macquart.**Limnophila rhenana n.sp.*

C'est la première fois, qu'une espèce de Limnophila a été signalée à Rott. Tête globulaire, petite; antennes à articles subcylindriques,

¹⁾ Löw H., Ueber den Bernstein und die Bernsteinfauna Meseritz 1850. und MEUNIER F., Monographie des Tipulidae de l'ambre de la Baltique. Ann. d. Sciences Nat. Paris 1908.

²⁾ Verhandelingen d. K. Akademie van Wetenschappen p. 15 (du tiré à part.), Amsterdam 1917.

³⁾ Bull. de la Soc. géol de France t. XIV p. 196, Paris 1914.

assez grêles et paraissant être plus courtes que la longueur du thorax ce dernier est gibbeux, et paraît avoir été orné de bandes ou facies longitudinales, les ailes de parfaite conservation permettent de donner les détails topographiques de la veination. Le radius est relié à la première nervure du secteur par une petite transversale (radius cross-vein), il y a 4 nervules qui sortent du secteur du radius; la médiane est simple, toutefois son secteur comprend 3 cellules, dont la première (M) n'est autre chose que la cellule discoidale des anciens auteurs. En définitive, de la dite cellule discoidale partent 3 nervures simples (chez la plupart des espèces de *Limnophila* la première de ces nervures est fourchue). La cellule discoidale est reliée par une transversale (radius-médiane cross vein) au cubitus qui est déjà fourchu à peu de distance de la base de l'aile. Le champ anal comprend 2 nervures simples.

Longueur du corps 8 mm. Longueur de l'aile 6 mm. Largeur de l'aile 2 mm.

L'abdomen assez allongé est composé de segments très distincts, malheureusement l'oviducte de la ♀ est peu appréciable.

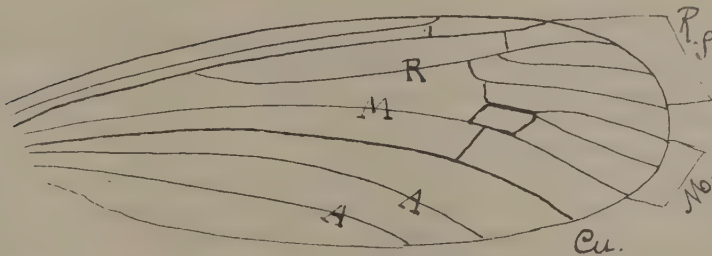


Fig. 3. Aile de *Limnophila rhenana* n. sp.

Phoridae.

Les diptères de cette famille, bien représentés, dans le succin de la Baltique¹⁾ dans les schistes miocéniques de Florissant et dans le copal subfossile de Zanzibar n'ont pas encore été signalés des feuillets ligniteux de Rott. Le genre *Phora* n'a pas encore été remarqué dans l'ambre sicilien.

Genre Phora, Meigen.

Phora sp?

La fossilisation empêche de donner un nom spécifique à ce diptère. On constate toutefois que le 3^{ème} article des antennes est disciforme

¹⁾ Löw., H. Ueber den Bernstein und die Bernsteinfauna Meseritz 1850.

MEUNIER, F. Monographie d. Leptiden u. Phoriden des Bernsteins Jahrb. d. k.k. preuss. geol. Landesanstalt Berlin 1909.

et qu'il paraît cilié et que le chète est aminci à l'extrémité. Les pattes sont robustes, leurs caractères sont trop noirs pour décider, si ce diptère appartient au genre *Aphiochaeta* Brues.

Longueur du corps 2 mm.

Coll. BAUCKHORN, Siegburg.

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(Communicated at the meeting of September 29, 1923).

§ 1. *Introduction.* The significance of extending the investigation on the magnetisation of paramagnetic substances to the temperatures obtainable with liquid helium, that might be expected a priori, has been confirmed in a convincing way by the preliminary research

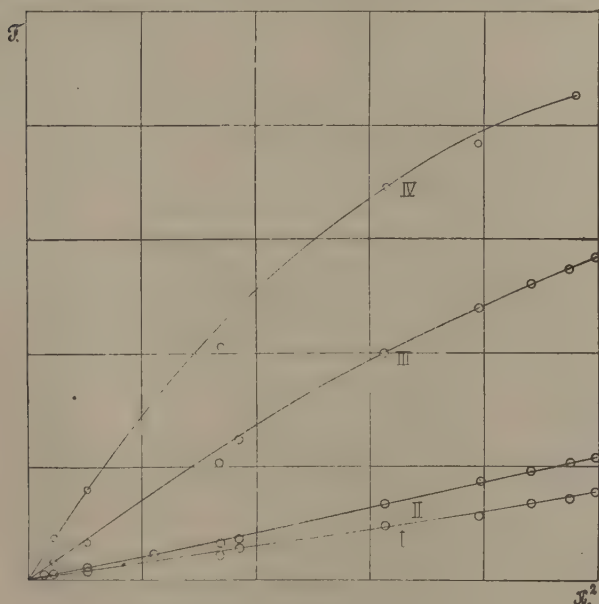


Fig. 1.

on the magnetisation of gadolinium sulphate in liquid helium carried out by KAMERLINGH ONNES in 1914¹⁾. The results then obtained showed the interest of continuing the research on gadolinium sulphate and completing the preliminary qualitative results by more accurate quantitative ones. Other substances, such

as the paramagnetic chlorides²⁾ presented themselves also for investigation in helium. However, closer inspection of the work of 1914 showed, that it was of little use repeating the work without detailed investigation

¹⁾ H. KAMERLINGH ONNES, these Proceedings, 17 p 283; Leiden Comm. N°. 140d. Cf. also idem, Rapport Solvay 1921, p. 131. Leiden Comm. Suppl. N°. 44a.

²⁾ l. c. p. 154, resp. p. 25.

of the method, more accurate calibrations and study of the corrections. E. g. concerning the direct results of the observations the considerable deviations¹⁾ from the proportionality between the force (F) and the square of the magnetic force between the poles of the electromagnet occurring at hydrogen temperatures (cf. fig. 1, taken from the paper mentioned) are particularly striking and, if the results are given in terms of LANGEVIN'S theory of paramagnetic gases (cf. fig. 2, taken from Leiden Comm. Suppl. N°. 44a) it may be asked whether no systematic errors occurred.

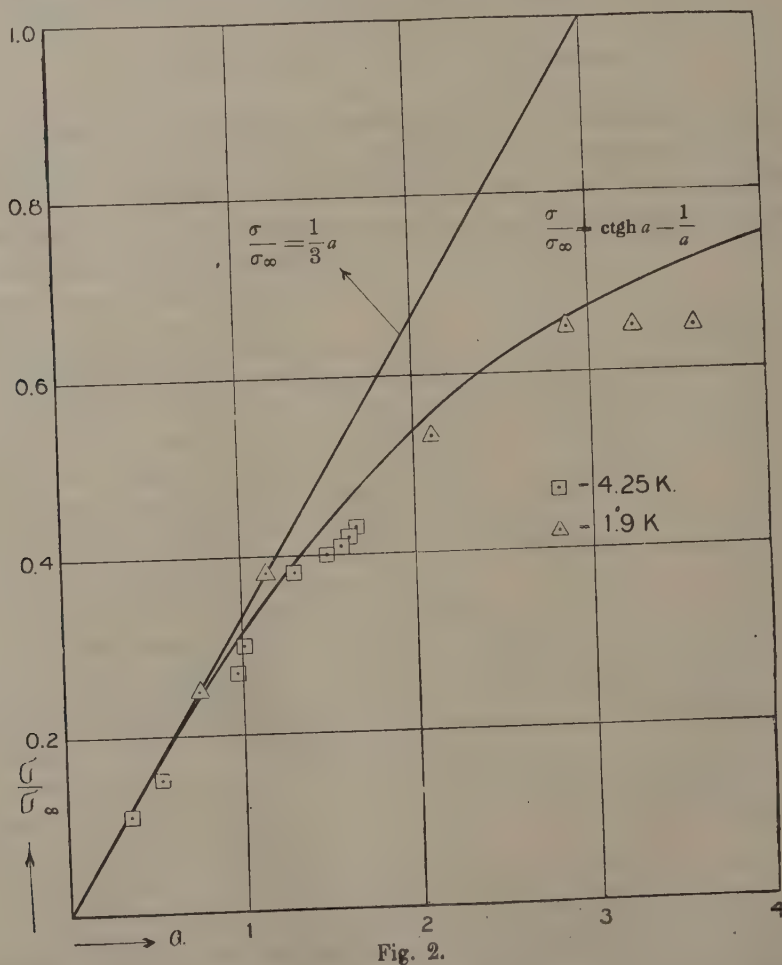


Fig. 2.

The method for measuring the magnetisation, its sources of errors

¹⁾ In the paper these deviations have been mentioned as probably due to inaccuracy in the topography.

and its corrections form the subject of the following paragraphs; we will consider more especially the topographic calibration of the electromagnet. It was carried out partially by means of the investigation of gadolinium sulphate in liquid hydrogen and so it furnished new material for the knowledge of the susceptibility of this substance, confirming old results. This new material will be communicated at the same time.

§ 2. *Apparatus and method.* The magnetisation was calculated from the force exerted by an inhomogeneous magnetic field on a small quantity of the material. For the measurement of the force the same apparatus was used as in the investigation of gadolinium sulphate in 1914, except a small alteration in connecting the tube containing the substance under consideration. At that time no description was given, so now some details may be mentioned. The apparatus was constructed by Mr. G. J. FLIM, chief of the Technical Department of the Cryogenic Laboratory, mainly on the same principles as the apparatus of KAMERLINGH ONNES and PERRIER¹⁾ for the investigation of paramagnetic substances. The substance to be investigated is placed at the bottom part of a long rod, the "carrier". This carrier is suspended to one or two floats swimming on mercury. The force exerted by the magnetic field on the substance is compensated by a known force and the compensation is checked by means of a telescope and a scale attached to the carrier (*Sc.* fig. 3). Some modifications were required with a view to the special circumstances. The apparatus is introduced at the top of the helium cryostat (*C*) and is supported by the rim *R*. It is counterbalanced by weights acting on the connecting tube between cryostat and liquefactor. The weight of the apparatus has been minimised. Partially for this purpose the ringshaped trough of the apparatus of KAMERLINGH ONNES and PERRIER has been replaced by a small glass reservoir (*G*) with only one float (*Dr*). The comparatively large forces occurring in the experiments (up to about 200 gr.) induced to prefer magnetic compensation instead of electrodynamic compensation by two coils, though the accuracy was diminished thereby. The compensating force comes from the attraction exerted by a current of suitable intensity passing through a coil *D* at the top of the apparatus on a weak iron rod *S* at the top of the carrier; by putting rings (*Ri*) under the coil *D* its height can be taken such as to exert upward or downward forces, as appears convenient. The distance of the weak iron rod to the interferrum of the electro-

¹⁾ These Proceedings 16, p. 689 and 786. Leiden Comm. N°. 139a.

magnet has been chosen such that the action of the latter on the former may be neglected.

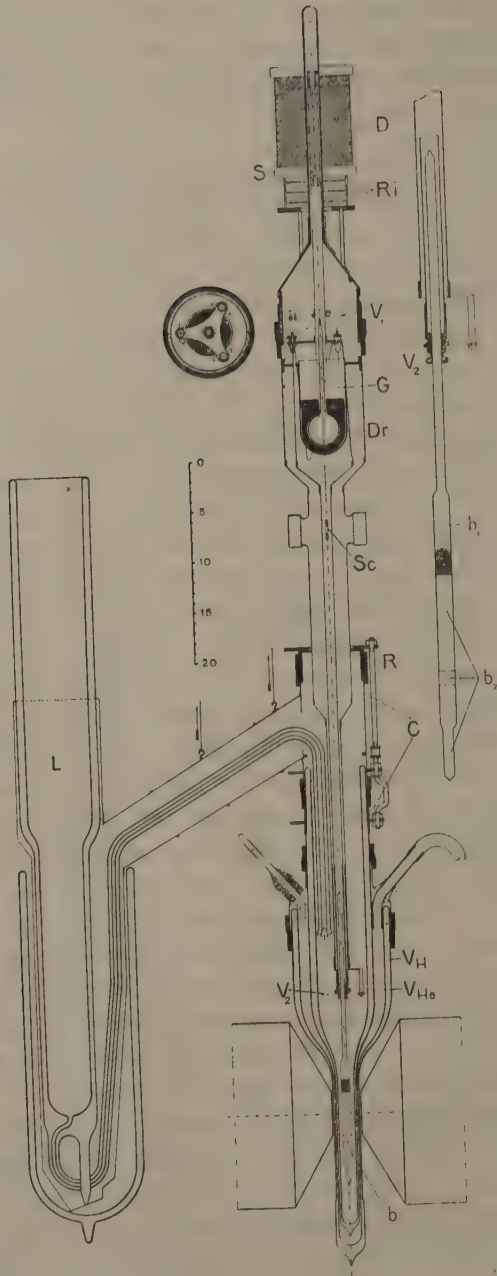


Fig. 3.

The tube (*b*, cf. the diagram of this detail in fig. 3) containing the magnetic substance, has been made and placed to obtain a symmetrical distribution of glass with respect to a horizontal plane passing through the centres of the poles of the electromagnet. In this way the attraction exerted by the magnet on the glass has been minimised and may be neglected. The dimensions have been chosen such that the sample is at the place of maximum $\frac{\partial H^1)}{\partial z}$, if the tube has been placed symmetrically in the field. The lower part (*b*₂) of the tube has been evacuated, in the upper part (*b*₁) a small quantity of helium gas has been introduced in order to improve the temperature equilibrium of the powder and the surroundings and of the particles of the powder mutually. The substance is enclosed between two glass disks, one of which has been melted on the tube, the other is free but is kept in its place by a small plug of cotton wool. Two flattened spiral springs, *P*₁, *P*₂ prevent a lateral displacement of the carrier. The lower one has been attached to the carrier and not, as in previous work, to the tube, so that the tubes may be replaced without changing the position of the carrier.

The end faces of the large size Weiss magnet have a diameter of 4 cm and are 26,5 mm apart. The semi-angle of the coneshaped boundary faces is 60°.

The compensating force as function of the intensity of the current in the coil *D* has often been determined as carefully as possible by suspending weights to the tube. Notwithstanding all precautions unexplained differences subsisted between the different calibrations. The extreme ones differ about 2 %. In calculating a series of observations use was made of the mean of the calibrations "before" and "after".

The specific magnetisation, σ , is calculated from the force measured by means of the relation

$$F g = m \sigma \frac{\partial H}{\partial z}, \quad (1)$$

where *F* represents the force (in grammes) exerted on the mass *m*. The *z*-coördinate is measured along a vertical from the middle of the interferrum; *H* is the magnetic force at the point indicated by *z*; $g = 981.3$.

¹⁾ If the susceptibility does not depend on the field strength, the maximum of $\frac{\partial H^2}{\partial z}$ is preferable. [Note added in the translation].

In every set, i. e. every measurement of the force corresponding to a definite value of the magnetic field and a definite temperature, the intensity of the current in the coil D necessary to bring the carrier into a chosen zero position was read the magnetic field being "of" and "on". These readings were taken for both directions of the currents in the coil and in the magnet.

§ 3. *Corrections, auxiliary measurements and sources of errors.*

a. Forces on the carrier without sample. These forces appeared to be not quite negligible and they increased with decreasing temperature. Investigation of the different parts of the apparatus showed that those forces were caused especially by a small screw at the bottom of the carrier (near V_2). The comparatively large increase of these forces when the temperature falls from 20° to 14° K. is very striking, e. g. 70 amp. passing through the electromagnet the attraction amounts to

0,259	gr.	at atmospheric temp.
0,326	„	20° K.
0,350	„	14° „

This is not what would be expected if the brass of the screw mentioned contained iron as an impurity. Further, such a comparatively very large increase in the liquid hydrogen region would give reason of suspecting much larger forces in the range of helium temperatures. However, they are then not large as appears from there being no systematic difference between the observations in which the mentioned parts of the carrier were certainly below and those in which they were certainly at some distance above the liquid helium level ¹⁾. Particular circumstances prevented determining those forces (whose comparatively large increase in the hydrogen region appeared firstly afterwards) at helium temperatures and in the light of the foregoing remark it seemed not absolutely necessary. In the following observations the correction for the forces on the carrier without sample has been applied for the hydrogen temperatures only.

b. Correction for demagnetisation. This correction may attain considerable values at the temperatures of liquid helium. In the case of a sphere of a homogeneous substance of density d in a homogeneous field the demagnetising field is $-\frac{4}{3}\pi\sigma d$. In our experiments the circumstances did not correspond exactly to these conditions. The sample is a powder in the shape of a small cylinder

¹⁾ Cf. the following communication § 3 note.

and is placed in an inhomogeneous field. Dr. BREIT¹⁾ has made a careful investigation in the case of a powder. According to him a first approximation for the demagnetisation is obtained if the formula mentioned is applied, taking for d not the density of the powder itself, but of the substance. If necessary this correction has been applied in that manner.

c. Topographical corrections. $\frac{\partial H}{\partial z}$ is in first approximation proportional to the field strength in the middle of the interferrum: H_0 . The factor of proportionality was calculated from a ballistic topographical calibration of the magnet²⁾. At currents of 10 and 20 amp. no appreciable difference in the topography was stated and for $z = 2.45$ cm. ($\frac{\partial H}{\partial z}$ being there a maximum) was found:

$$H = 0.815 \cdot H_0, \quad \frac{\partial H}{\partial z} = 0.199 \cdot H_0 \quad (2, 3)$$

If however for gadolinium sulphate³⁾ the force F' is calculated as a function of H_0 , no proportionality of F' to H_0 ² is found, as might be expected on account of previous measurements⁴⁾ (apart from small corrections if LANGEVIN's formula is followed) but deviations occur up to 20 %. This appears from table I and fig. 4. To the observed value of F , given in the third column now first a correction for the demagnetisation is applied: F is multiplied by $1 + \frac{4}{3} \pi d_0 \chi$; according to the remark *b* (see above), d_0 is taken equal to 3⁵⁾, for χ , the specific susceptibility, the value following from the un-corrected measurements has been taken. At 20°.42 K. this correction is 1.2 %, at 13°.98 K. 1.8 %. In the column headed L the corrections for the deviations according to LANGEVIN's formula have been given. With those two corrections an apparent Curie-constant $C' = \chi T$ has been calculated.

The values found for C' appear to be strongly dependent on the field strength (cf. fig. 5). This may not be due to errors in the

¹⁾ These Proceedings 25, p. 293; Leiden Comm. Suppl. N°. 46.

²⁾ The calibration really refers to a pole distance of 26 mm., not to 26.5 mm., the distance occurring in the experiments described.

The parameters of this field do not belong to those for which FORRER has given so much and such important data (J. FORRER, thesis Zürich, 1919).

³⁾ The gadolinium sulphate, $Gd_2(SO_4)_3 \cdot 8H_2O$, originated from the supply previously kindly sent by Prof. URBAIN. Two tubes have been filled with it, Gd I and Gd II, containing resp. 0.4735 en 0.4414 gr. of gadolinium sulphate.

⁴⁾ H. KAMERLINGH ONNES and E. OOSTERHUIS, these Proceedings 15, p. 322 § 6, Leiden Comm. N°. 129b, § 6.

⁵⁾ P. GROTH, Chem. Krystallographie II (1908), p. 460.

calibration of the magnetic field. This calibration may be estimated to be accurate to a few thousands. The deviations must be caused by the circumstance that at large and at small values of H_0 the proportionality mentioned may not be expected to hold ¹⁾.

TABLE I.

Gadolinium sulphate II ($m = 0,4414$ gr.)								
$T = 20^{\circ}.42$ K.								
Nr.	I	F	H_0	L	$10^2 C'$	q	$10^2 C$	$\frac{(C - C_m)}{C}$
4	5 amp.	0.81 gr.	3295	0.0	2.100	1.018	2.064	+1.7%
5	5	0.80						
6	10	3.10	6605	0.1	2.015	0.997	2.021	-0.45
3	15	6.98	9875	0.2	2.031	1.000	2.031	0.0
7	20	12.00	12940	0.4	2.038	1.005	2.028	-0.1
2	30	20.66	17320	0.8	1.962	0.963	2.037	+0.3
8	30	20.56						
9	45	25.99	20235	1.2	1.820	0.897	2.029	-0.1
1	60	28.17	21600	1.4	1.729	0.856	2.021	-0.45
10	60	28.00						
$T = 13^{\circ}.98$ K.								
15	4	0.74	2627	0.1	2.093	1.026	2.040	+0.5
16	5	1.13	3295	0.1	2.032	1.018	1.996	-1.7
14	10	4.52	6605	0.2	2.025	0.997	2.031	0.0
13	20	17.41	12940	1.0	2.046	1.005	2.036	+0.3
17	20	17.39						
18	30	29.32	17320	1.9	1.942	0.963	2.017	-0.7
12	45	37.36	20235	2.6	1.826	0.897	2.036	+0.3
11	60	40.33	21600	3.0	1.739	0.856	2.033	+0.1
19	60	40.44						
20	70	41.77	22230	3.2	1.701	0.835	2.037	+0.3

¹⁾ In fig. 2 the points for the higher field strengths show the same kind of deviation from the LANGEVIN curve at $4^{\circ}.25$ K. as at $1^{\circ}.9$ K. In my opinion this fact is caused by the absence of proportionality mentioned in the text.

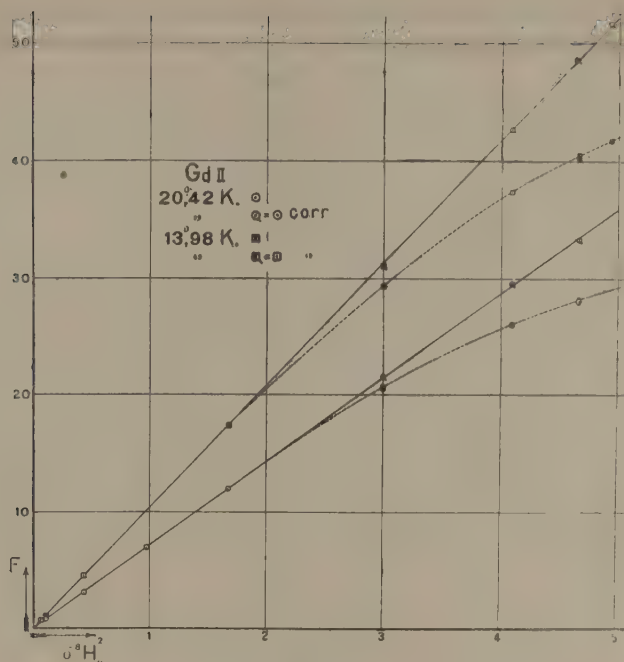


Fig. 4.

We have put:

$$\left. \begin{aligned} H &= s \cdot 0.815 \cdot H_0 \\ \frac{\partial H}{\partial z} &= r \cdot 0.199 H_0 \end{aligned} \right\} \dots \dots \dots (4)$$

$$q = s \cdot r \dots \dots \dots (5)$$

and for 15 amp. $q = s = r = 1$.

The quantities q , s and r are called the topographical corrections.

The apparent Curie-constant C' is connected to the true Curie-constant C by the formula: $C' = qC$ and does not depend on the temperature. Fig. 5 shows that within the limits of accuracy of the experiments at both hydrogen temperatures¹⁾ the same values for C' are found. Only at 5 amp. ($H_0 = 3295$) where the forces are small and the measurements less accurate there exists a larger deviation.

The values for C' have been smoothed graphically and then the topographical correction q has been determined from $q = \frac{C'}{C_{15 \text{ amp.}}}$.

In the column $10^2 C$ the value of $10^2 C'$ corrected with q has been

¹⁾ The circles refer to 20.42 K., the squares to 13.98 K.

given and in the last column the difference (in percents) of $10^3 C$ with the mean value 2,030.

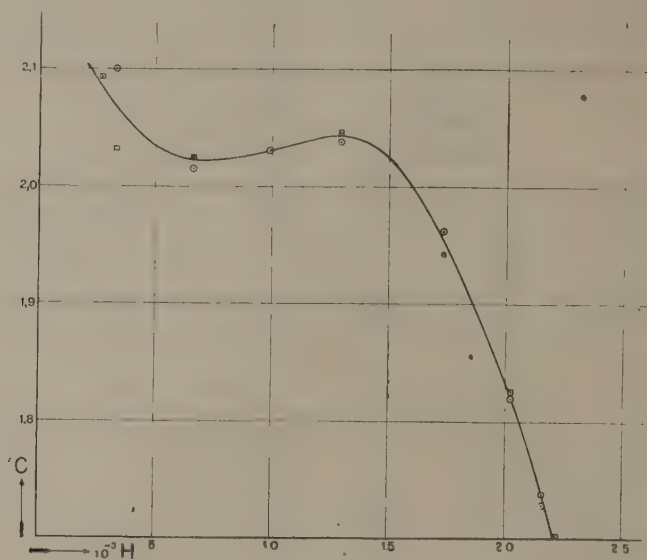


Fig. 5.

r was determined from experiments on the attraction of two small ellipsoids ¹⁾ of Swedish Carbon iron placed as well as possible at the same spot as the substances in the actual experiments. Use was made of the measurements of STEINHAUS und GUMMICH ²⁾ on the relation between field strength and magnetisation when saturation is nearly reached, the so called law of approach

s was calculated from formula (5). The values found for r and s have also been smoothed graphically ³⁾.

In these determinations the distribution of magnetism on the pole faces of the magnet has been supposed to be perfectly rigid ⁴⁾.

¹⁾ Masses 30.0 and 32.0 mg., major axis 6.2 mm., minor axis 1.1 m.m.

²⁾ Ber. d. Physik Ges. 17 (1915) p. 271.

³⁾ This causes the product of the given r and s to be not exactly equal to q .

⁴⁾ Cf. P. WEISS, J. de Phys. May 1910 and P. WEISS and H. KAMERLINGH ONNES, Leiden Comm. N^o. 114, p. 16.

Strictly speaking: for a magnet current of 15 amp. the distribution of magnetism on the pole faces of the magnet has been supposed to be perfectly rigid and as regards the other current intensities it has only been supposed to be the same for gadolinium sulphate at hydrogen temperatures and for the S.C. iron ellipsoids. In fact, the magnetic moments are of the same order in both cases (though the volumes on which they are distributed are different); in the case of gadolinium sulphate at *helium* temperatures they are much larger, yet the same values of r and s have been applied (cf. next communication) [Note modified in the translation].

So the values given in table II have been found.

d. Corrections for diamagnetism of the liquid bath and of the anion could be left out of consideration.

e. As regards the *accuracy* and the *sources of error* may firstly be pointed out that the *helium temperatures* are rather uncertain, especially the lower ones. There was no room for a special stirrer and so the liquid could be stirred only so much as was possible by moving the floating system up and down. Therefore probably the temperature was not always evenly distributed and not perfectly well defined. This is especially important at temperatures below the maximum of density; then the cooling at the surface by evaporation does not give rise to downward convectional currents. However the lower temperatures are not only somewhat indefinite, but the values accepted are not very accurate. They have been determined graphically by means of the total existing material for helium vapour pressures¹⁾, but this leaves at the temperatures between 1° and 3° K. uncertainties of the order of 0,1 of a degree.

TABLE II.

Pole distance 26.5 mm.; $s = 2.45$ cm.		
I	r	s
3 amp.	0.973	1.062
4	0.983	1.044
5	0.990	1.030
10	0.999	1.003
15	1.000	1.000
20	0.995	1.002
30	0.960	1.010
45	0.893	1.021
60	0.837	1.030
70	0.808	1.035

f. Much care was bestowed on the *adjusting* of the *sample* to the proper place in the magnetic field, or more accurately, of the adjusting of the magnet to the sample, the cryostat not being movable.

¹⁾ H. KAMERLINGH ONNES and SOPHUS WEBER, these Proceedings 18, p. 493; Leiden Comm. N°. 147b; H. KAMERLINGH ONNES, Leiden Comm. N°. 159 p. 35.

Once the magnet was adjusted in its place, it was marked by means of two plummets suspended to the cryostat and marking two pointers on the yoke of the magnet, for the magnet had temporarily to be removed to afford opportunity of bringing the DEWAR vessels V_{He} and V_H (fig. 3) into place. The large magnet is very heavy and there was no device for moving the magnet slightly in horizontal direction, so the horizontal adjustment was accompanied by great difficulties and possibilities for inaccuracy.

During the operations with liquid helium and liquid hydrogen the cryostat, forming one whole with the liquefactor, moved slightly in an irregular way as a consequence of the changing temperature circumstances in the different parts. By means of pulling rods the initial position with respect to the magnet was restored.

As far as the adjustment in vertical direction is concerned, it must be pointed out that the distance (at atmospheric temperature) from the centre of the mass to the centre of the field is considered as "place" of the sample in the magnetic field. This place determines the values of the constants in formulae (2)—(5). In the measurements in liquid hydrogen and in liquid helium this place has changed really by the shortening of the carrier in consequence of its cooling. The influence on $\frac{\partial H}{\partial z}$ will be very small as $\frac{\partial H}{\partial z}$ is maximum, but for the same reason the influence on H has to be taken into consideration. In itself there is reason for a correction. In the (rather unfavorable) case that the carrier up to 20 cm above the sample has the temperature of the boiling point of liquid hydrogen and the other part is at atmospheric temperature, a shortening of 0,3 mm would follow from the data of CH. LINDEMANN.¹⁾ H would be 0,006 H_0 smaller than corresponds to formula (2) i. e. about 0,7 %. Yet no correction has been applied, because it would have required an accurate determination of the place of the substance during the measurements as the sinking of the liquid level changed the temperature distribution along the carrier and thus the place of the sample. Moreover in the measurements in liquid hydrogen and in liquid helium (and the experiments only refer to these temperatures) the correction is nearly equal when the liquid level is on the same height, as the expansion coefficient at these low temperatures rapidly decreases to zero.

g. Finally it must be mentioned that no trace has been observed of the powder particles getting directed or remaining directed by the magnetic forces.

¹⁾ Physik. Zs. 13, (1912), p. 737.

§ 4. *The Curie constant of gadolinium sulphate.* In § 3c it has been mentioned already that for *Gd* II $2,030 \times 10^{-2}$ has been found.

For the Curie constant of *Gd* I we find:

$$\begin{array}{lll} T = 20^{\circ},31 \text{ K.} & \chi = 1,0566 \cdot 10^{-3} & C = 2,146 \cdot 10^{-2} \\ T = 14^{\circ},68 & \chi = 1,4663 \text{ ,,} & C = 2,152 \\ & \text{mean:} & 2,149 \end{array}$$

The measurements on *Gd* I have been considered as less accurate than those on *Gd* II, because (cf. § 3f on the difficulties of the adjustment) the tube appeared afterwards for unknown reasons to be not exactly in the middle between the pole faces, but 1,6 mm out of the center. A previous determination of the Curie-constant of *Gd* I quite independent of the present research had given $2,113 \times 10^{-2}$. So it is not very probable that the large difference between the Curie constants of *Gd* I and *Gd* II is due to inaccurate adjustment of the tube only. Besides it must be remarked that different observers have found values differing more still than the values mentioned: from the results of Mlle FEYTIS¹⁾, KAMERLINGH ONNES and PERRIER²⁾, and KAMERLINGH ONNES and OOSTERHUIS³⁾ the Curie-constant of gadolinium sulphate is found to be⁴⁾.

$$\text{Mlle FEYTIS} - 2,167 \cdot 10^{-2}$$

$$\text{K. O. and P. } 2,086$$

$$\text{K. O. and O. } 2,016.$$

These differences are not yet explained.

Finally, I wish to express my sincere thanks to Professor KAMERLINGH ONNES for his kind interest in my work.

¹⁾ Paris C. R. 153 (1911), p. 668.

²⁾ These Proceedings 14, p. 115; Leiden Comm. N^o. 122a.

³⁾ " " 15, p. 322; Leiden Comm. N^o. 129b.

⁴⁾ A correction has been applied for the diamagnetism of the crystal water and of the anion. The first correction had been applied already by Mlle FEYTIS.

Physics. — “*Further experiments with liquid helium. T. Magnetic researches. XXIII. On the magnetisation of gadolinium sulphate at temperatures obtainable with liquid helium.*” By H. R. WOLTJER and H. KAMERLINGH ONNES. (Communication N°. 167c from the Physical Laboratory at Leiden).

(Communicated at the meeting of September 29, 1923).

§ 1. *Introduction.* Previous¹⁾ preliminary researches and a detailed discussion²⁾ of the results then obtained have shown the importance of a closer investigation of the magnetisation of gadolinium sulphate at very low temperatures: this substance is one of the comparatively few, that follow CURIE'S law down to the region of temperatures obtainable with liquid hydrogen. Now in the light of LANGEVIN'S theory the CURIE law holds only approximately, viz. as long as the susceptibility may be considered to be independent of the field strength: LANGEVIN gives for the ratio of the specific magnetisation, σ , to the specific saturation magnetisation, σ_∞ ,

$$\sigma : \sigma_\infty = \cotgh a - \frac{1}{a} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

$$a = \frac{\sigma_{m\infty}}{R} \cdot \frac{H}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1b)$$

($\sigma_{m\infty}$ being the saturation magnetisation of one gram molecule, R the gas constant per grm. mol., H the magnetic field applied and T the absolute temperature).

For small values of a

$$\sigma : \sigma_\infty = \frac{1}{3} a \quad \text{or} \quad \chi = \frac{\sigma}{H} = \frac{\sigma_\infty \cdot \sigma_{m\infty}}{3R} \cdot \frac{1}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If T is small and thus a large, χ is no longer independent of H , but the curve $\sigma : \sigma_\infty = f(a)$ deviates from the straight line $\sigma : \sigma_\infty = \frac{1}{3} a$, becomes concave towards the a -axis and approaches asymptotically to $\sigma : \sigma_\infty = 1$ (cf. fig.) The detailed discussion of the preliminary experiments has already made very probable the existence

¹⁾ H. KAMERLINGH ONNES, these Proceedings 17, p. 283; Leiden Comm. N°. 140d.

²⁾ H. KAMERLINGH ONNES, Rapport Solvay 1921, p. 131; Leiden Comm. Suppl. N°. 44a. I.

of deviations of this type. Yet it is not to be expected a priori that LANGEVIN's theory would be followed in this case, for this theory has been deduced for a gas with perfect rotational freedom of the molecules and starts from the assumption of the equipartition of energy in all degrees of freedom. Now the case of powdered gadolinium sulphate at low temperatures does not correspond to either of these assumptions. It is true that LANGEVIN's theory has been extended by WEISS¹⁾ to powdered crystals, but WEISS confines himself to small values of the parameter α ; on the other hand EHRENFEST²⁾ has developed a theory in which the relation (2) is obtained for crystal powders on the assumption of the existence of quanta but then the saturation magnetisation is only half the value corresponding to perfect parallelism of all elementary magnets and in the preliminary experiments a higher value seemed to be reached.

Confirmation and extension of the preliminary results was thus very desirable; the same method has been followed as in the previous work: the specific magnetisation, σ , is calculated from the force F (in grammes) exerted on the mass m by an inhomogeneous magnetic field with aid of the formula $Fg = m\sigma \frac{\partial H}{\partial z}$. A detailed study of the apparatus, the corrections and the sources of error, a comprehensive account of which has been given in the preceding communication³⁾, has made it possible to attain a much greater accuracy than in the previous work, at least as far as the magnetic measurements are concerned. The determination of the temperature from the vapour pressure of the bath is still a weak point, especially since the vapour pressure law is as yet not sufficiently well known⁴⁾. The research relates to the same tubes, *Gd I* and *Gd II*, that have served for the research in liquid hydrogen and that have been mentioned in the preceding communication (§ 3c).

§ 2. *Observations.* The direct results of the observations may be given first: tables I and II (I being the number of ampères in the magnet coils; H_0 the field strength, in gauss, in the centre; F the force in grammes, on the total mass of substance).

With *Gd II* between the points N°. 15 and N°. 28 points have been left out in which the observations have been taken at increas-

1) P. WEISS, Paris C. R. 156 (1913) p. 1674. According to O. STERN (Zs. f. Phys. 1 (1920) p. 147) WEISS' deduction is not sound.

2) P. EHRENFEST, these Proceedings 23, p. 989; Leiden Comm. Suppl. N°. 44b.

3) H. R. WOLTJER, these Proceedings p. 613; Leiden Comm. No. 167b.

4) I. c. § 3c.

TABLE I.

Gadolinium sulphate I						
Date	Vapour pressure	T	Nr.	I	H_0	F
March 1 st , 1923	761 mm. ¹⁾	4°.20 K.	1	30	17320	90.14
"	"	"	2	20	12940	55.26
"	"	"	3	10	6605	15.76
"	"	"	4	5	3295	3.89
"	"	"	5	5	3295	4.01
"	"	"	6	15	9875	33.83
"	"	"	7	30	17320	89.94
"	"	"	8	60	21600	114.76
"	"	"	9	70	22230	117.81
"	"	"	10	45	20235	109.54
"	"	"	11	30	17320	90.96
"	360 mm	3°.53 "	12	70	22230	136.93
"	"	"	13	45	20235	123.42
"	"	"	14	30	17320	103.78
"	"	"	15	20	12940	65.61
"	"	"	16	10	6605	19.04
"	"	"	17	5	3295	4.76
"	"	"	18	5	3295	4.75
"	"	"	19	15	9875	40.26
"	"	"	20	30	17320	102.54
"	"	"	21	60	21600	129.12
"	"	"	[22	70	22230	130.68
"	100 mm.	2°.73 "	[23	70	22230	152.27]
"	"	"	24	45	20235	148.13
"	"	"	25	30	17320	121.71
"	"	"	26	20	12940	79.75
"	"	"	27	10	6605	24.36
"	"	"	[28	5	3295	6.12]
"	763 mm.	4°.20 "	29	30	17320	91.11
"	9.5 mm.	1°.66 ₅ "	30	70	22230	173.70
"	4 mm.	1°.48 "	[31	60	21600	173.41]

¹⁾ The difference between international and local m.m. mercury (these Proceedings 21 p. 658 note 2; Leiden Comm. No. 152d p. 47, note 4)) is here of no importance.

TABLE II.

Gadolinium sulphate II						
Date	Vapour pressure	T	Nr.	I	H_0	F
April 13 th , 1923	761 mm.	4° .20 K.	1	60	21600	108.27
"	"	"	2	30	17320	85.67
"	"	"	3	15	9875	32.44
"	"	"	4	5	3295	3.74
"	"	"	5	5	3295	3.77
"	"	"	6	10	6605	15.10
"	"	"	7	20	12940	53.00
"	"	"	8	30	17320	85.80
"	"	"	9	45	20235	102.76
"	"	"	10	60	21600	108.04
"	300 mm.	3° .40 "	11	30	17320	98.48
"	39 mm.	2° .30 "	12	30	17320	119.86
"	4 mm.	1° .48 "	13	30	17320	133.53
"	"	"	14	60	21600	152.29
"	"	"	15	30	17320	133.59
"	759 mm.	4° .20 "	28	30	17320	85.48
"	2.9 mm.	1° .41 ₅ "	29	70	22230	156.36
"	"	"	30	45	20235	152.69
"	"	"	31	30	17320	136.30
"	"	"	32	5	3295	10.20
"	"	"	33	4	2627	6.46
"	"	"	34	3	1960	3.68
"	1.7 mm.	1° .31 "	35	70	22230	157.74
"	"	"	36	60	21600	157.72

ing pressure in order to test whether temperature corresponded to pressure, the only stirring possible being made by the moving up and down of the carrier¹⁾. The magnetisations observed pointed to much lower temperatures than corresponded to the actual pressures and thus to a large temperature lag. Therefore these points have been left out of consideration.

§ 3. *Discussion.* For *Gd II* 0,02024²⁾ has been accepted as Curie-constant and with this value σ_{∞} and $\sigma_{m\infty}$ have been calculated according to formula (2). Half the real molecular weight has been used in calculating $\sigma_{m\infty}$ from σ_{∞} , as the atoms of *Gd* are assumed to have rotational freedom. This is usually done for salts containing more than one metal atom in the molecule³⁾; moreover, if the whole molecular weight had been taken, $\sigma_{m\infty}$ would have become $\sqrt{2}$ larger, σ_{∞} $\sqrt{2}$ smaller and thus $\sigma:\sigma_{\infty}$ again $\sqrt{2}$ larger and one would have found values larger than 1, as for $\sigma:\sigma_{\infty}$ the value 0.84 has been attained (Cf. table IV).

We find:

$$\sigma_{m\infty} = 434,2 \times 10^3 \text{ (38.65 WEISS-magnetons).}$$

$$\sigma_{\infty} = 116,25.$$

For the Curie constant of *Gd I* we found⁴⁾

$$C = 0,02149$$

$$\sigma_{m\infty} = 447,4 \cdot 10^3 \text{ (39.82 WEISS-magnetons)}$$

$$\sigma_{\infty} = 119,79.$$

From the tables I and II $\sigma:\sigma_{\infty}$ and α have been calculated for *Gd I* and *Gd II*, with its own particular Curie constant for each substance. The results have been collected in tables III and IV. The values placed in square brackets are a priori less reliable, mostly because during or immediately after the measurement the gadolinium sulphate appeared to be not sufficiently below the liquid helium level⁵⁾. The differences between the observed values of $\sigma:\sigma_{\infty}$ and

¹⁾ I.e. § 3e.

²⁾ Cf. the preceding communication § 4, where on account of a later somewhat modified calculation 0,02030 has been given. The difference is of no importance.

³⁾ P. WEISS, Arch. d. Sc. phys. et nat. (4) 31 (1911).

B. CABRERA, J. de Chim. Phys. 6 (1918) p. 442, especially p. 462.

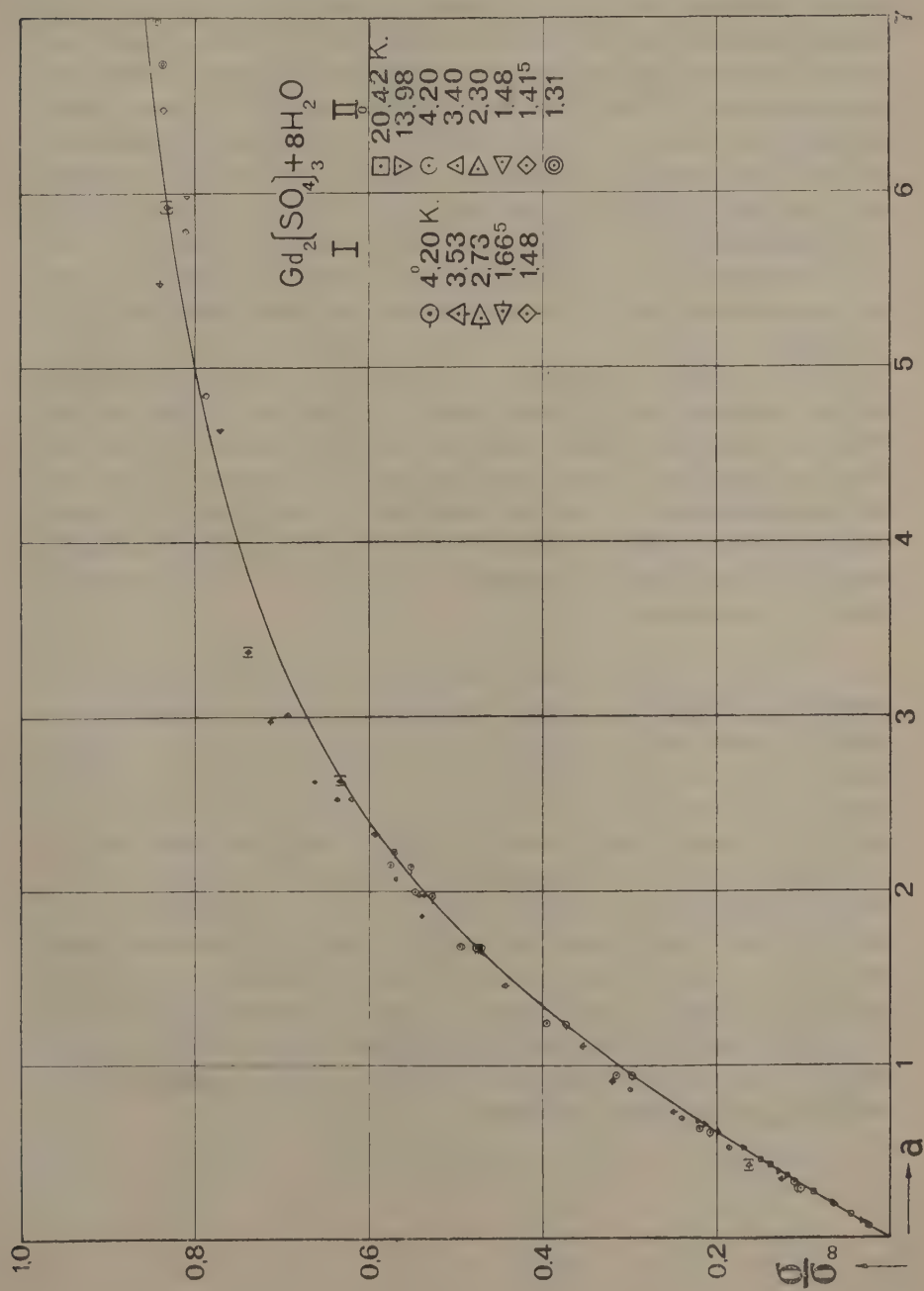
⁴⁾ Cf. the preceding communication § 4, where the difference between both results has been discussed.

⁵⁾ At the points marked with an asterisk the helium level was certainly below the spring V_2 (cf. the preceding communication § 3a). Though a general tendency to higher values of $\sigma:\sigma_{\infty}$ (cf. the diagram) must be acknowledged to exist, there is no systematic difference between the points with and without asterisk.

TABLE III. Gadolinium sulphate I.

<i>I</i>	4° 20 K.				3° 53 K.				2° 73 K.				1° 66½ K.				1° 48 K.			
	Nr.	<i>a.</i>	$\left(\frac{b}{g} \middle \frac{b}{g}\right)_{obs.}$	$100 \cdot \frac{O-C}{O}$	Nr.	<i>a.</i>	$\left(\frac{b}{g} \middle \frac{b}{g}\right)_{obs.}$	$100 \cdot \frac{O-C}{O}$	Nr.	<i>a.</i>	$\left(\frac{b}{g} \middle \frac{b}{g}\right)_{obs.}$	$100 \cdot \frac{O-C}{O}$	Nr.	<i>a.</i>	$\left(\frac{b}{g} \middle \frac{b}{g}\right)_{obs.}$	$100 \cdot \frac{O-C}{O}$	Nr.	<i>a.</i>	$\left(\frac{b}{g} \middle \frac{b}{g}\right)_{obs.}$	$100 \cdot \frac{O-C}{O}$
5	4	0.2888	0.1036	+ 7.6	17*	0.3384	0.1268	+11.7	[28*	0.4267	0.1630	+13.8]								
"	5	0.2882	0.1068	+10.5	18*	0.3384	0.1266	+11.6												
10	3	0.6174	0.2075	+ 3.2	16*	0.7246	0.2508	+ 6.9	27*	0.9162	0.3208	+ 9.8								
15	6	0.9408	0.2977	+ 0.4	19*	1.106	0.3544	+ 3.6												
20	2	1.239	0.3732	— 0.8	15*	1.458	0.4430	+ 3.2	26	1.857	0.5384	+ 5.0								
30	1	1.675	0.4710	— 1.0	14*	1.976	0.5425	+ 1.7	25	2.528	0.6362	+ 3.0								
"	7	1.675	0.4700	— 1.2	20*	1.977	0.5360	+ 0.5												
"	11	1.673	0.4753	0.0																
"	29*	1.673	0.4763	+ 0.2																
45	10	1.970	0.5269	— 1.0	13	2.328	0.5936	+ 0.7	24	2.975	0.7124	+ 6.1								
60	8	2.140	0.5516	— 1.7	21*	2.529	0.6209	+ 0.6												
70	9	2.223	0.5702	— 0.6	12	2.624	0.6627	+ 5.0	[23	3.371	0.7369	+ 4.2]	30*	5.475	0.8406	+ 2.8				
"					[22*	2.631	0.6824	+ 0.3]												

the values calculated according to LANGEVIN's formula, expressed in percents of the observed value, are given in the columns headed $100 \cdot \frac{O-C}{O}$.



It cannot be denied that while on the one hand, one gets the strong impression that LANGEVIN's formula is followed (cf. the figure, in which the LANGEVIN curve and the observed points have been drawn), on the other hand the deviations are larger than was anticipated. However they may be explained from the sources of error. Besides all that has been said in the preceding communication as to the accuracy, it must be pointed out that the larger deviations occur especially at the lower field strength values, where the topographical corrections are rather uncertain and also the measurements of the field strength less reliable. Further, the magnetic moment acting at the very low temperatures is so large that the assumption of a rigid distribution of the magnetism on the pole faces (and on this assumption the field measurements and the determination of the topographical corrections are more or less based) certainly holds no longer.

Moreover it must be observed, that errors in σ_{∞} and in H_0 exert on the abscissae an influence opposite in direction to that on the ordinates and thus appear greater in the diagram. Taking all these circumstances into account, especially also the uncertainty of the demagnetisation, it may be concluded, that powdered gadolinium sulphate follows LANGEVIN's formula down to about 1°3 K; thus it seems possible to use the magnetic susceptibility of gadolinium sulphate in thermometry.

§ 4. *Results.* The specific magnetisation of powdered hydrated gadolinium sulphate has been investigated for the temperatures of liquid hydrogen and liquid helium. It appears that though the fundamental assumptions to LANGEVIN's theory do not apply, yet LANGEVIN's formula is followed. For the parameter a of LANGEVIN's theory the value 7 has nearly been reached. The highest magnetisations obtained are about 84 % of the magnetisation corresponding to perfect parallelism of all elementary magnets. This result is independent of the uncertainties in the temperature and the value of the demagnetising field. So it appears that Prof. EHRENFEST's theory is here not applicable without further extension, since this theory (which is based on quanta assumptions and holds, contrary, to LANGEVIN's theory, directly for crystal powders) gives for the saturation magnetisation only 50 % of the value mentioned.

Physiology. — *"The string galvanometer in wireless telegraphy".*

By W. F. EINTHOVEN. (Communicated by Prof. W. EINTHOVEN).

(Communicated at the meeting of March 24, 1923).

The string galvanometer, as is well known, consists of a conducting fibre stretched like a string in a strong magnetic field. A current passing through the fibre induces a displacement of it in a plane perpendicular to the lines of magnetic force. The deflection can be observed with a microscope and the magnified image can be photographed.

Many attempts have been made to use this instrument for the reception of wireless signals, but only ordinary models, with a relatively long, not very much stretched string have been tried, and these show great sensitiveness towards disturbing direct currents. The wireless signals were received in such a way that the high frequency oscillations were rectified by means of some device, and the rectified current impulses were passed through the string; this was affected in the same way as when conveying a true direct current.

But, used in this way, the string galvanometer has only brought disappointment in wireless telegraphy, for it reacts to every current of some duration with the same sensitiveness, and even the smallest atmospherics are sufficient to give trouble. Some large Companies, who have tried to use the string galvanometer at their transatlantic stations, have abandoned work with it.

The application here to be described of the instrument is based on a quite different method¹). The incoming high frequency oscillations are not rectified but are sent through the string immediately. The string is short and stretched so much, that its own period corresponds to the period of the ether waves used in wireless signalling. Choosing the length of the string conveniently and adjusting its tension, we can bring it in tune with practically all continuous waves available in radio-telegraphy. If for instance these have a length of 1 kilometer corresponding to 300.000 periods per sec., the string is adjusted so that the proper frequency of its vibrations is also 300.000 per sec.

¹) Patented.

The length of the string, being about 10 millim. for waves of (for instance) 10 kilom., is only 1 millim. for waves of 1 kilom. We have also experimented with shorter strings showing a still higher frequency of their proper vibrations. Heretofore as far as we know it has not been possible to induce these frequencies in any mechanism.

The string, for which we take a fine quartz fibre, is rendered able to conduct by cathode bombardment, and stretched between two microscopes; one of these serves to concentrate the light, the other to project the image, whilst both microscopes, in order to obtain a sharp definition of the string, must be very near to one another. The objectives, having a numerical aperture of 0,95, are no more than 0,2 millim. away from the string. Since the front lens of such an objective has a diameter larger than the length of the string, a special device is necessary to fix the string; this is done in such a manner that the rays of light are not intercepted, and the full angle of aperture of the objectives is made use of efficiently.

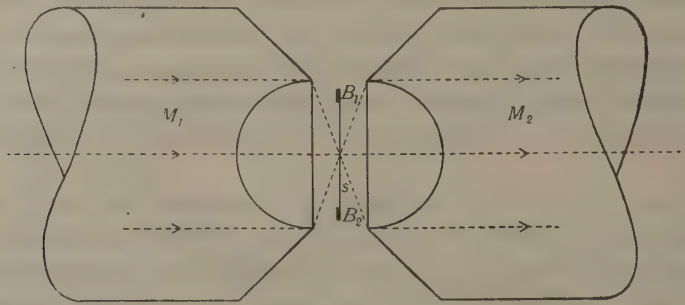


Fig. 1.

Diagram of the string s between both of the microscopes M_1 and M_2 .

B_1 and B_2 , fine metal strips to which the string is soldered. The direction of the rays of light is indicated by the dotted lines and arrows.

The difficulty was overcome by soldering both ends of the string to fine metal strips placed in the optical plane perpendicular to the string, and rigidly attached to the apparatus in order to tighten and slacken the string.

It is important to have the string vibrating as freely as possible. Therefore it has not only to be fine but also strongly stretched like a string of a piano or a violin. Its minute mass per unity of length causes it to suffer a strong damping effect from the air, and this must be avoided. Therefore the space around it is evacuated, and in order to make the vacuum efficient it has to be made high. We

attained vacua of 1μ Hg and even higher and were able to show, that under such conditions the air damping has practically no more influence on the movement of the string. The vibrations do not die away more slowly when the vacuum is made higher than 1μ , since the internal friction of the string itself, i. e. the fact that the material of the string has no perfect elasticity is another cause of damping.

It is not to be expected, that the vibrations of a coated quartz fibre stretched like a string would die away as slowly as those of a pure quartz rod which has been fixed at only one end. Experiments of HABER and KERSCHBAUM¹⁾ have shown that it took more than 12 minutes, before the amplitude of a quartz rod vibrating in vacuo was diminished to one half of the original size. LANGMUIR²⁾ succeeded in lowering the pressure in an incandescent bulb lamp so much that the time of halving the amplitude was lengthened to nearly two hours.

But if we cannot make the vibrations of our string die away equally slowly, nevertheless for the purpose aimed at the result is satisfactory. We could for instance show, that a string performing 40.000 vibrations per sec., without the intentional application of a damping factor needed a time $\tau = 0,65$ sec. to diminish its amplitude in the proportion of $1 : \frac{1}{e}$, wherefrom it may be inferred, that the logarithmic decrement of the movement amounted to 4×10^{-5} , conf. fig. 2.



Fig. 2.

A string the vibrations of which are dying away freely.

$$\lambda = 7,5 \text{ km}, \tau = 0,65 \text{ sec.}, \delta = 4 \times 10^{-5}.$$

This decrement is of the greatest value for our purpose, for the smaller it is so much the better is the selectivity of the instrument. If the string has been put in tune with a definite wave, it will react to atmospheric disturbances and to currents of different wave lengths coming in from other stations so much the less, the smaller the decrement is. Generally speaking we may say that the efficiency of a receiving apparatus is determined by the amount of its decrement.

For purposes of comparison it may be recalled, that the smallest

¹⁾ Zeitschr. f. Elektrochemie. Bd. 20, 1914, p. 296.

²⁾ Journal of the American Chem. Soc. 35, 107 (1913) cited from HABER u. KERSCHBAUM.

available decrement of an electric circuit is about 0,01 and that in most cases this value is higher. The decrements of all the receiving apparatus known to us, which mechanically register the signals are larger than that of the string galvanometer.

However it is only possible to profit fully by a small decrement,

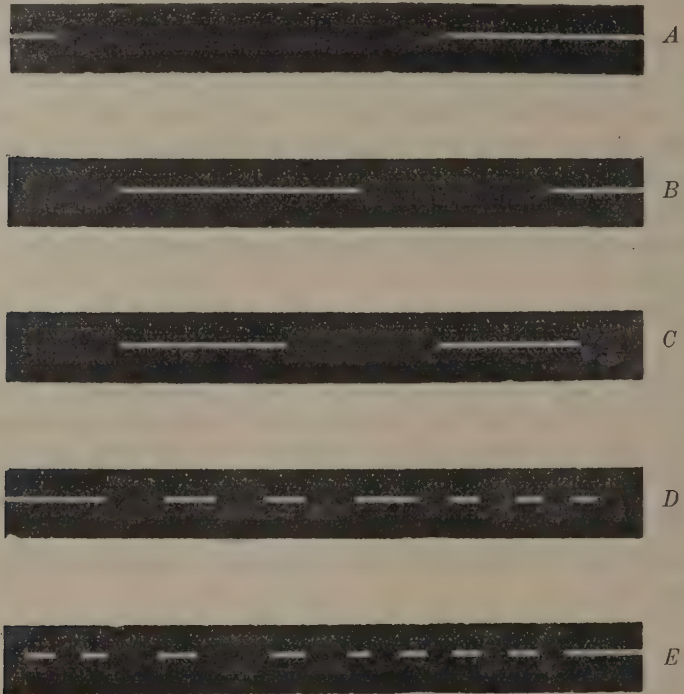


Fig. 3.

	Field magnet current	τ	δ
<i>A</i>	0,5 Amp.	0,27 sec.	$9,25 \times 10^{-5}$
<i>B</i>	1,— "	0,1 "	$0,25 \times 10^{-3}$
<i>C</i>	2,— "	0,03 "	$0,83 \times 10^{-3}$
<i>D</i>	4,— "		$3,— \times 10^{-3}$
<i>E</i>	6,— "		$6,2 \times 10^{-3}$

when signalling is excessively slow. Signals coming in at the usual speed would be intermingled if the vibrations of the string died away so slowly. Therefore it is necessary to increase the decrement

of the receiver purposely. This is not performed by admitting air around the string. On the contrary the vacuum is kept as high as possible in all experiments, but the strength of the magnetic field is changed. By varying this value from zero to a maximum the amount of the decrement can be adjusted in a simple and at the same time very precise manner.

In the above fig. 3 the photos are reproduced of the same string as that of fig. 2 the strip of paper moving with the same velocity, i. e. 10,75 millim. per sec. Continuous waves the length of which was 7,5 kilom. were coupled inductively with the circuit of the string, and switched on and off repeatedly, whilst in the successive photos the current exciting the field-magnet was increased from 0,5 to 6 Amp. The photos show, that the time in which the vibrations of the string die away is shorter as the exciting current increases. The decrements can only be measured in the photos *A*, *B* and *C* because of the low speed of the paper strip. For *D* and *E* they have been calculated from the intensity of the magnetic field, which amounted tot 7600 and 10.900 Gauss respectively.

In the calculations of all useful decrements in radio-telegraphy, the proper decrement of the string itself caused by its internal friction is to be neglected, whilst in a high vacuum also the air damping is not to be taken into account. Under these circumstances the relation between the decrement and the field intensity is given by the formula

$$\sigma = \frac{4}{\pi_1} \cdot \frac{H^2 \times 10^{-9}}{m w N} \quad (1)$$

where σ represents the logarithmic decrement,

H the intensity of the magnetic field in GAUSS,

m the mass of the string in grams per centim.,

w The resistance of the galvanometer circuit in OHMS per centim.,

N the number of periods per sec. of the string when vibrating in resonance with the continuous waves induced.

When receiving a signal the decrement must be adjusted so that the dots and dashes of a signal only just begin to blend, as may



Fig. 4.

Record of signals from an Italian station, made in Leyden. The decrement of the string has been adjusted so that the dots and dashes of a signal only just begin to blend.

Although our only receiver was a small, not very favourable aerial, we were able repeatedly to take long telegrams, the signals of which came in absolutely clear.

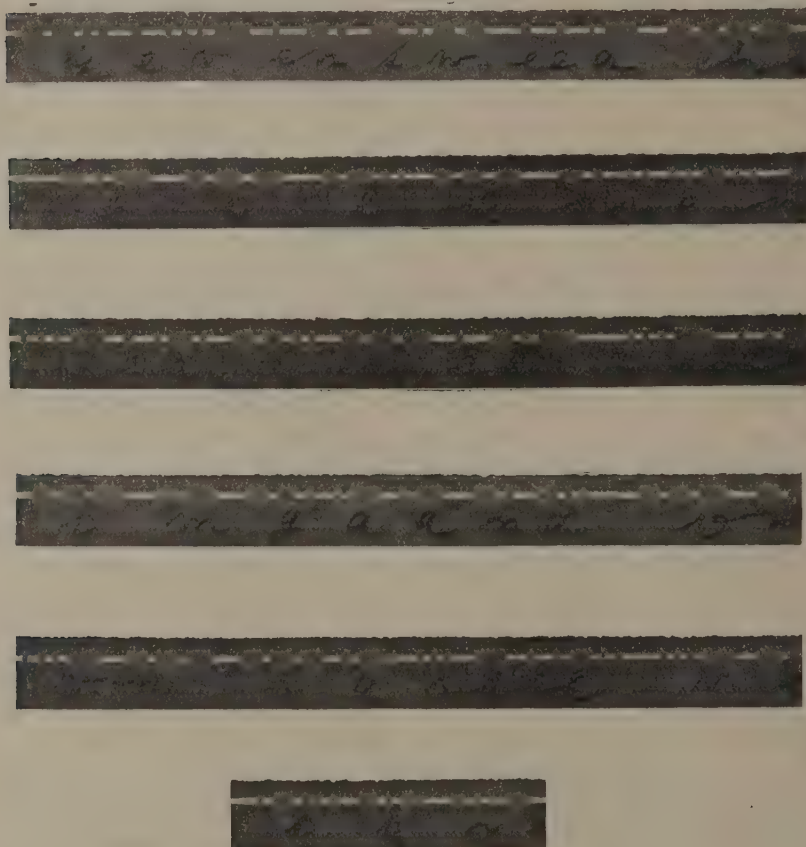


Fig. 5.

Record of signals from the alternator on the Malabar at Bandoeng,
made in Leyden January 13th, 1923.

To what extent can the reception by means of the galvanometer stand comparison with the ordinary telephone reception?

In order to answer this question we shall first compare the sensitiveness of the two instruments. The human ear is a very sensitive organ. According to MAX WIEN¹⁾ it is sufficient to apply to the tympanic membrane an energy amounting to 0.83×10^{-12} ergs

¹⁾ MAX WIEN. Ueber die Empfindlichkeit des menschlichen Ohres für Töne verschiedener Höhe. PLÜGER's Arch. f. d. ges. Physiol. Bd. 97, S. 1.

per sec. that is a power of $0,83 \times 10^{-19}$ watts, in order to produce a sensation of sound; the necessary amplitude of the air waves being a thousand times smaller than the diameter of a molecule. In accordance with this the telephone is capable of responding audibly to very weak currents. The modern telephones, now much in use in wireless telegraphy, which are put in tune with the most favourable note for perception by the human ear, are to be considered among the most sensitive of all existing instruments.

MAX WIEN ¹⁾ states that for the most sensitive telephone under most favourable conditions a power of $3,03 \times 10^{-14}$ watts is wanted to produce a just barely audible sound. AUSTIN ²⁾ indicates a 60 times smaller value viz. $0,5 \times 10^{-15}$ watts.

To evaluate the sensitiveness of the galvanometer we suppose that during the reception of a signal a uniform effective electromotive force E be applied to the terminals of the string. At the first moment when the string is still in rest, it will be traversed by a maximum current $I = \frac{E}{W}$, where W represents the ohmic resistance of the string, but gradually the current will decrease by the back-electromotive force which is set up in the string by its movement. If we neglect the internal friction in the string itself and make the vacuum so high, that it may be considered as absolute, the back-electromotive force produced will be equal to E as soon as the end-amplitude is attained. The current flowing through the string then $= 0$. As long as the signal lasts the string goes on oscillating in tune with it without consuming energy.

For evaluating the sensitiveness we have to take the maximum number of watts wanted i.e. $\frac{E^2}{W}$. If the string have a mass of M grams, being in tune with N cycles per sec., and its electromagnetic decrement being σ_{em} , the number of watts wanted to induce an end-amplitude of U cetim. is

$$B = \frac{\pi^2}{2} \times 10^{-7} \times M U^2 N^2 \sigma_{em} \quad . \quad . \quad . \quad (4)$$

or also

$$B = \frac{4500 \pi^2 M U^2}{\lambda^2 \tau}, \quad . \quad . \quad . \quad (5)$$

¹⁾ WIEDEMANN's Annalen 4. IV, 1901, p. 450.

²⁾ Jahrbuch der drahtl. Telegr. 11 and 12, 1916. „Conf. also H. O. TAYLOR. Telephone receivers and radio telegraphy. Proceedings of the institute of Radio engineers, 1918, Vol. 6, p. 37.

where λ represents the wave-length in kilometers, and τ the time in seconds necessary to raise the amplitude of the oscillations of the string from 0 to a value $\left(1 - \frac{1}{e}\right)$ of the end amplitude. The speed of transmission admissible is inversely proportional to τ .

The minute amount of energy sufficient to keep the string oscillating with its end-amplitude can easily be evaluated. For the sum of the values neglected previously, can be determined by measuring the decrement of the vibrations when dying away freely.

Denote this decrement with σ_{l+s} then the value to be found is

$$B_1 = \frac{\pi^2}{2} \times 10^{-7} \times MU^2 N^2 \sigma_{l+s} \dots \dots \dots (6)$$

or also

$$B_1 = B \times \frac{\sigma_{l+s}}{\sigma_{em}} \dots \dots \dots (7)$$

where σ_{l+s} is again supposed to be small in comparison with σ_{em} . This is always the case with a good string, a moderate field and an attainable vacuum. Under the conditions of the figures 2 and 3 we have $\sigma_{l+s} = 4 \times 10^{-5}$, whilst σ_{em} with a magnetizing current of 4 amp. attains a value which is 75-times larger viz. 3×10^{-3} and therefore $B_1 = 0,0133 B$.

What value is to be computed for B when use is made of formula (4)? The result depends on the dimensions, especially on the diameter of the string inserted in the galvanometer.

If we take a fine string¹⁾ with a diameter of $0,2 \mu$, a vibration amplitude of the same dimension will already be visible and suitable to be recorded. We have then $U = 2 \times 10^{-5}$ centim. The mass of a string of the above mentioned diameter and of 1 centim. length may be taken as $M = 2 \times 10^{-9}$ grams. Suppose, moreover, $N = 20.000$, and $\sigma_{em} = 0,001$, then we find, for the number of watts wanted, that $B = 3,2 \times 10^{-15}$. From this we infer, that the sensitiveness of the galvanometer is to be evaluated to an amount of the same order of magnitude as that of the telephone.

The use of such fine strings is attended with certain practical difficulties, so that we prefer to work with strings 5 to 6 times thicker and therefore considerably less sensitive. Moreover the sensitiveness decreases, when the wave-length is shorter and the speed of transmission higher, as may be seen from formula (5).

¹⁾ Conf. W. EINTHOVEN, Ueber die Beobachtung und Abbildung dünner Fäden. PFLÜGER's Archiv. f. d. ges. Physiol. Bd. 191, S. 60.

However, in view of the comparison between string and telephone it may be pointed out, that the maximum sensitivity of the latter named instrument is by no means available in radio practice, for there is a great difference between the intensity of a signal just barely audible and one which is readable.

It will be noticed that we only have compared the power sensitiveness of the galvanometer and of the telephone as such, and that the application of these instruments in combination with the oscillating audion and with low and high frequency amplifiers has been left out of consideration. For the sensitiveness of reception by telephone in combination with the oscillating audion we may refer to the paper of Austin ¹⁾. He mentions that for a just audible signal the absolute sensitiveness of the oscillating audion is $1,2 \times 10^{-15}$ watts, that is to say a power, which is about 2,5 times greater than that needed by the telephone as such.

For the practical use of the string galvanometer in radio-telegraphy it is superfluous to try to obtain the greatest possible sensitiveness of the instrument. It is not the sensitiveness which determines its usefulness, since weak signals may be strengthened by means of amplifying vacuum tubes without limit. The efficiency of a receiver is much more determined by its selectivity i.e. its freedom from disturbances.

If we wish to compare the reception by the galvanometer to that by the telephone from the point of view of their selectivities, we must discuss once more the properties of the human ear. As is well known we are able to distinguish by means of hearing many sounds produced simultaneously. If we pay special attention to one of the numerous musical instruments of a complete orchestra, we are able to follow its performance separately. So also the Marconist can distinguish the tone of a signal, although many other sounds or noises of, for instance, extraneous stations or atmospheric disturbances reach him at the same time. This secures for reception by telephone an important advantage over every form of reception which has the object of recording the signal graphically. In the graphical image of a concert of sounds it is extremely difficult to follow the tone which we wish to analyse and often it will be even quite impossible to do so.

But against this disadvantage of the galvanometer there is the

¹⁾ LOUIS W. AUSTIN. The measurement of radio-telegraphic signals with the oscillating audion. Proceedings of the Institute of Radio engineers, 1917, Vol. 5, p. 239.

advantage of a much smaller decrement, and we may ask how far in practice advantage and disadvantage are counterbalanced.

The answer depends on the possibility of deriving the full profit from the small decrement of the receiver. Let us for instance try to receive in Leyden the signals of the present high frequency alternator at Bandoeng. It does not keep its wave of 7,5 kilom. absolutely constant, but according to our measurements the wave varies by amounts of 1 to 2 per thousand. If, by diminishing the field intensity, we decrease the string decrement so much as would be desirable when receiving a constant wave, a signal would only be received now and then, that is to say only at those moments, when the varying wave of the transmitter coincides exactly with the wave to which the string is put in tune. To different wavelengths the string does not respond, so that the dots and dashes transmitted are not received regularly and the telegram becomes unreadable. We are obliged to increase the string decrement and so to enable the reception of a greater range of variation of the wave-length of the transmitter.

On experimenting we obtained the impression that the reception by telephone of the high frequency alternator of Bandoeng is disturbed by extraneous noises about as much as the reception by the galvanometer. In both cases practically as many signals become unreadable by atmospherics. But we have not yet had the opportunity to carry out exact measurements on this point and it may be noticed, that the difference in skill of the various Marconists, who are carrying on the comparative experiments must also be allowed for.

If the wave transmitted oscillates still more than is mentioned above, the Marconist will obtain the better result, but if it is being kept steady, such as actually is the case with many modern transmitters, then the advantage will pass to the side of the galvanometer. The dots and dashes on the strip of paper will then be like those of fig. 4 and of the upper part of fig. 6.

The slower the rate of transmission so much the smaller the string decrement may be made; the freedom from disturbances becomes improved proportionately and thus the possibility of receiving with the galvanometer increases. On the other hand the Marconist is not able to take advantage of a more constant transmission wave; it is impossible for the human ear¹⁾ to perceive the minute variations in pitch, to which a string vibrating with a small decrement is capable of responding noticeably.

¹⁾ Practically also when the Marconist is applying beat reception.

But it is not only with a slow transmission that the string is superior. If, in relation to the disturbances, the signals are strong enough to make a record of them with a moderate or even a large string decrement, then high speeds of transmission will become possible and soon the Marconist will no more be able to read the signals, while the galvanometer is recording easily a few hundreds of words per minute.

Dr. DE GROOT of Bandoeng, to whom we are much indebted, has suggested a valuable idea. For his enthusiastic collaboration in the difficult experiments carried on at Bandoeng with the galvanometer some time ago, we thank him heartily here.

Dr. DE GROOT has suggested the application of two galvanometers simultaneously when an arc generator be used for transmission; one string may be put in tune with the active wave, the other with the wave of rest. An atmospheric appearing at a given moment may be easily recognized as such, if it influences the registration of only one of the two waves. Thus the possibility of making the signal readable throughout the atmospheric disturbances will become greater.

In fig. 6 a record is reproduced which has been made at Leyden according to the suggestion of Dr. DE GROOT. The string of one



Fig. 6.

Record of the arc generator *FL*, Paris with 2 galvanometers in parallel. The signalling wave is registered by one, the non signalling wave by the other galvanometer.

galvanometer is seen vibrating every time the other is standing still and vice versa. How great the practical value of this method will be has yet to be determined, but the first impressions which we have obtained from the result of a few experiments are favourable.

The idea of using 2 galvanometers simultaneously may find another application when signals are to be received, the wave-length of which is not very constant. Either string may be put in tune with a different wave; one with a wave which is a little longer, the other with a wave, which is a little shorter than the mean length around which the transmission wave is fluctuating. So the admissible range of fluctuation is increased, while the decrement of the vibrations of either string may remain small.

However, rather than applying this, after all, somewhat defective

means, it is better to try to improve the transmitter. As a matter of fact present technique is actually capable of producing transmitters which keep their wave practically constant.

The advantages of the reception by galvanometer in distinction from the reception by telephone are worth mentioning. On transmitting slowly it will be possible to receive signals with the galvanometer, which are not readable by telephone. Every improvement in this direction of the receiving apparatus, which always remains relatively simple, saves, as AUSTIN¹⁾ observes rightly, large sums needed both for the erection of high power sending stations and for their working expenses. And that, as matters stand at present, improvements are still wanted, is obvious from the many difficulties experienced even with the best installations. To quote an example it may be noticed, that during the whole of July 1921 the communication between two of the Trans-Atlantic stations, which are considered among the most reliable, was so poor that only 23 per cent of the words sent were successfully received²⁾.

The high speed reception with the galvanometer makes it possible to take full advantage of the installation at those hours of the day and the night, which are the most favourable for the transmitting of the signals, and to transmit many more words than could be received by telephone. Moreover the secrecy of the telegrams can be better secured since the numerous telephone-receivers will not be able to read the quick signals.

In time of war the interference by a second station will be hindered, when the signalling wave and the non signalling wave of an arc transmitter are received simultaneously with two galvanometers.

Finally we may mention another advantage which bears upon the general use of wireless telegraphy in the world. It is Dr. DE GROOT, who has placed it on the fore-ground. During night and day numerous signals are sent from many hundreds of transmitters. The installations interfere with one another, if they use waves the lengths of which do not greatly differ. The difference in wave-lengths which are applicable for transmitting signals is limited; only these waves are useful, which range neither below nor above a certain length; in other words: the spectrum of the useful waves is comparatively small. Everyone using a part of it takes it away from another man.

¹⁾ Conf. L. W. AUSTIN, Long distance radio communication. Journal of the Franklin Institute, Vol. 193, Apr. 1922, p. 437 (458).

²⁾ Conf. L. W. AUSTIN l.c. p. 443.

The smaller the part of the spectrum he uses, the larger the part which remains for others.

Owing to the small decrement of the galvanometer a wireless installation may be restricted to using a smaller part of the spectrum than heretofore, with the result that it will be possible to increase the number of simultaneously working installations. This increase is badly needed, so we may expect on good grounds, that the galvanometer will be capable of rendering a service to radio communication in general.

We do not finish this paper without rendering our tanks to the many persons who have been ready to help us with our work. Especially we wish to express our gratitude for the interest and the support, which we have received from Mr. Th. B. PLEYTE who was at that time our Colonial Minister.

Anthropology. — "*The Menarche in Dutch Women and its precipitated appearance in the youngest generation*". By Prof. L. BOLK.

(Communicated at the meeting of September 29, 1923).

With the aid of several physicians I have collected a number of data with regard to the menarche in Dutch women, about which nothing was known so far. In collecting these data the greatest accuracy has been observed and in this communication we have only made use of the cases, in which not only the year, but also the month of the first menstruation has been noted. Besides this the colour of hair and eyes of the various subjects had been stated, as I also wished to ascertain through this examination, whether the degree of pigmentation is of influence in the commencement of sexual maturity in the young girl.

Although it is not easy to obtain accurate data, I have succeeded in collecting 1800 reports of non-Jewish women as well as 165 of Jewesses.

On working out this material, several unexpected and surprising results came to light, which I will relate in succession, leaving the data obtained from the Jewesses until the end.

The first question which could be answered with the aid of these reports concerned the age at which the menarche appears in Dutch

TABLE I.

Age	Number	Percentage	Age	Number	Percentage
8 years	2		16 years	121	6.7
9 "	2		17 "	54	3.—
10 "	31	1.7	18 "	25	1.4
11 "	131	7.3	19 "	3	
12 "	302	16.7	20 "	2	
13 "	464	25.7	21 "	2	
14 "	408	22.6	22 "		
15 "	251	13.9	23 "	2	

women in general. It is well known that this age shows great individual variations, and this is also seen in the Table I, in which the actual numbers, as well as the relative percentage, have been stated according to the age.

In fig. 1 curve A shows, in percentages, its appearance at each separate age.

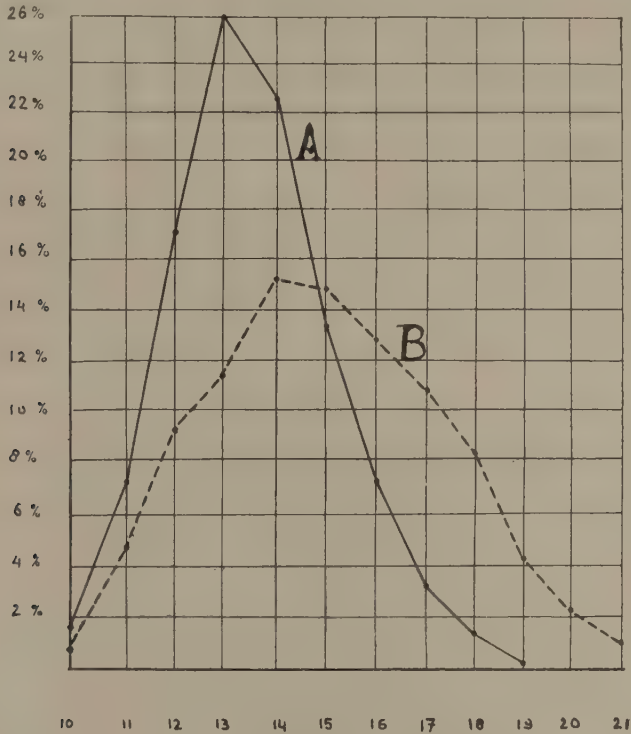


Fig. 1.

From this table and graph it appears that the beginning of the function of the sexual glands varies between the tenth and eighteenth year; it is true that in 4 cases the menses already appeared before the 10th year (8 years 2 mths; 8 y 12 m; 9 y 4 m; and 9 y 12 m), but these cases do not join regularly on to the variability-curve and may be regarded as abnormal precocity.

The variability-curve of the menarche begins as an unbroken line at the age of 10 years and 4 months, mounting continually after this. This mounting during the 10th and 11th year is to be seen in Table II, in which the number of cases per month during these years has been noted. I have inserted this table, as it shows that the earliest age at which the menarche, as a physiological pheno-

menon, begins, is actually the middle of the 10th year, so that when a girl has passed the age of ten-and-a-half years one cannot look upon the beginning of the menstrual process any more as a sign of pathological precocity, at most as a rapid development of the sexual glands.

TABLE II.

Age	Number	Age	Number
10 years 1 month	0	11 years 1 month	3
" " 2 months	0	" " 2 months	5
" " 3 "	0	" " 3 "	6
" " 4 "	1	" " 4 "	7
" " 5 "	2	" " 5 "	6
" " 6 "	3	" " 6 "	6
" " 7 "	2	" " 7 "	9
" " 8 "	2	" " 8 "	11
" " 9 "	3	" " 9 "	14
" " 10 "	7	" " 10 "	19
" " 11 "	6	" " 11 "	24
" " 12 "	6	" " 12 "	21

The beginning of the variation-curve in the middle of the tenth year is a sign that sexual maturity in our country can begin at a comparatively early age and the further course of this line confirms this fact, for it mounts rapidly to reach its top in the 13th year.

Sexual maturity made its appearance before the 12th year in 9% of the girls, before the 13th year in 26%, and in more than half before the 14th year. The average age of the menarche, taking the months into consideration as well, appears to be 13 years, 9 months and 15 days. If one compares this average with others mentioned in the literature, drawn from the population of Western Europe, then it appears that in our population of the present day the menarche, on an average, begins early.

This commencement, however, is dependent on so many external conditions, that if any conclusions are drawn from a comparison of these averages, this should be done with the greatest care.

As one of the internal influences determining the age of the menarche, the racial factor is usually mentioned. Several authors

deny this influence entirely, others attach great importance to it, which shows how difficult it is to determine whether the race is really of any influence on the menarche, as it also is influenced by other, external, factors, (social surroundings, temperature, soil, etc.).

I do not know of any investigation in which the influence of the race on the commencement of sexual maturity has been actually proved, and this induced me, while collecting the data, to inquire into the degree of pigmentation.

The material was sorted and divided into the women with light and those with dark eyes; these will in future be called "blondes" and "brunettes"; of the former my material contained 1130, of the latter 670.

The appearance of the menarche was worked out statistically for each of these groups separately, the result is seen in Table III and the graphs plotted out from this table have been sketched in fig. 2. in which curve A refers to the Jewesses, curve B to the "blondes", curve C to the "brunettes".

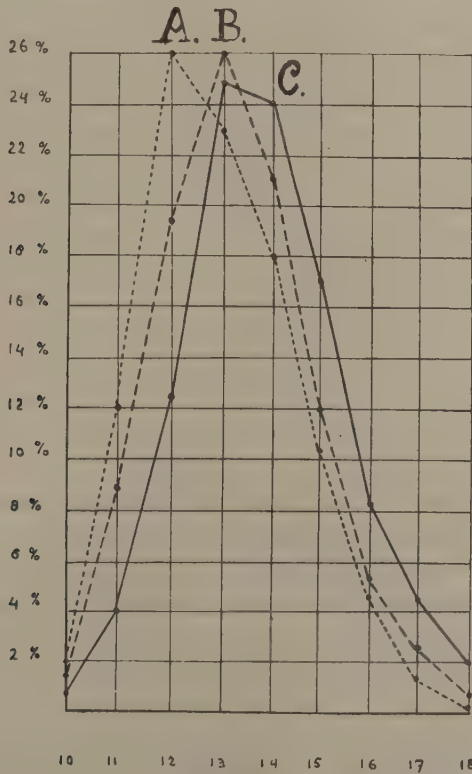


Fig. 2.

The result of this investigation into the relation between menarche and degree of pigmentation was surprising, as it was in contradiction with what one might expect. It is a well known phenomenon that the menarche appears at an earlier age in the dark-coloured races than in the fair ones. Most writers ascribe this to climatic influences, especially to the high temperatures in which the dark-skinned races live.

TABLE III.

Age	Blondes		Brunettes	
8 years	1		1	
9 "	1		1	
10 "	22	1.8 ‰	9	1.3 ‰
11 "	104	9.1 "	27	4 "
12 "	220	19.5 "	82	12.3 "
13 "	294	26 "	170	25.2 "
14 "	244	21.5 "	164	24.6 "
15 "	136	12.1 "	115	17.2 "
16 "	65	5.7 "	56	8.5 "
17 "	26	2.3 "	28	4.3 "
18 "	12	1 "	13	2 "
19 "	1		2	
20 "	2		—	
21 "	1		1	
23 "	1		1	

I myself, however, conjectured that the racial factor would be of importance here and that an earlier appearance of the menarche would be a biological characteristic of the more pigmented races.

It appears, however, from the data given in Table III that for the Dutch population the contrary holds good; it is just the fair types which, in comparison to the dark ones, are characterized by an earlier maturity.

The difference is even considerable, for while 56.4 % of the girls of the fair type have come to maturity before their 14th year, this is only the case in 42.8 % of the dark type. As one can, however,

see from the graph and from Table III, the beginning of the variability-curve lies for both types in the 10th year; in the "brunettes" this begins at 10 years 5 months, in the "blondes" at 10 years 4 months; so for both groups what one can designate as the threshold-age of sexual maturity, is the same. After this beginning the curve for the fair type mounts more rapidly than for the "brunettes"; the end of the normal variability, however, is the same for both types, and lies in the 18th year.

The exact difference between both groups appears from the following average figures, which have again been calculated including the months:

Average age of menarche in "blondes": 13 years, 5 months, 17 days; in "brunettes": 14 years, 4 months, 5 days. So this makes a difference of full 10 months between both types.

A difference of this sort, and in a contrary direction to what I had expected, is very remarkable. As we have to do here with two groups of people living in the same circumstances, which excludes external factors which might influence the menarche, this difference must be entirely regarded as the result of an internal factor, and it is only the racial factor which can be taken into consideration here.

The light-eyed component of our population belongs, in general, to the race which peoples the North of Europe, the "*Homo nordicus*", while the brown-eyed, which constitutes about a third part of the Dutch people, as is proved by a former investigation of mine, belongs to the race inhabiting the centre of Europe, the "*Homo alpinus*".

It appears, therefore, that a lesser development of the pigment is accompanied by an acceleration of the sexual development. The relation between both phenomena is, however, not so simple; which can be seen from the fact that the average age of the menarche in the more strongly pigmented Jewesses, is earlier than in the "blondes".

The activation of the sexual sphere of the developing individual is dependent on very many factors; and, in considering the difference which has come to light, we must not forget the possibility that the racial factor which is here at work, could be of a psychological instead of a physiological nature. The blonde as well as the brunette girl has reached the threshold-age of maturity on arriving at the age of 10-and-a-half years. (Later on it will appear that this also holds good for the Jewish girl). The time which passes for each individual between this age and the activation of the sexual functions, is determined by a number of external and internal factors, and among the latter we leave room for the special psyche of each race.

Thus far on the average age of the menarche in the Dutch

population in general; I will now proceed to another result of my investigation, which was as surprising as it was unexpected.

It had attracted my notice, while working out my material, that the older people mentioned therein were often characterized by a late appearance of the menarche. This observation gave rise to the question whether the menarche could have undergone some change during the last decades, in such a manner that sexual maturity in the youngest generation begins, on an average, at an earlier age than in the former generations. I have tried to find an answer to this question in two ways. In the first place I collected from my material data referring to persons born before 1880, and calculated from these the average age of the menarche. Secondly I tried to obtain data relating to the menarche in mother and daughters. Especially this last is difficult, considering the fact that only a very few of the women can actually mention the year of the menarche, much less the month. Yet I have succeeded in collecting a number of such data.

Both ways led to the same result, viz. that the menarche in what we may call the youngest generation, as regards sexual maturity, arrives at a considerably earlier period than formerly. I will return to the cause and significance of this phenomenon after communicating the pure facts.

Let us begin with the menarche in women born before 1880. In my material concerning them there were 98 data of the menarche according to year and month, and furthermore I possessed 104 cases in which only the age was mentioned. These 232 cases have been systematically arranged in Table IV, and curve *B* in fig. 1 gives the direction in percentages for each age.

If one compares Table IV with Table I, the following will be seen: the beginning of the variability-curve lies, for women of the

TABLE IV.

Age	Number	Percentage	Age	Number	Percentage
10 years	2	0.8	17 years	27	11.2
11 "	12	5.—	18 "	19	8.1
12 "	21	9.—	19 "	10	4.3
13 "	27	11.2	20 "	5	2.2
14 "	37	15.9	21 "	4	1.3
15 "	35	15.1	22 "		
16 "	31	13.3	23 "	2	0.8

older generations, also in the 10th year. This fact confirms the opinion already mentioned above, that the middle of the 10th year is the physiological threshold-age of sexual maturity in woman.

Opposite to this very constant starting-point of the variability-curve stands the most changeable ending-point. This falls in the older generations in the 21st year, in contrast to the 18th in the younger generation. The top of the curve, which in the latter individuals lies in the 13th year, has been shifted to a higher age in the older generations and lies in the 14th and 15th year.

From this it already appears that formerly the phase of sexual latency, after crossing the threshold-age, lasted considerably longer in a great many girls than nowadays. This also follows from the fact that, as shown in Table I, more than 50 % of the youngest generation menstruates before the end of the 13th year, while of those born before 1880 this was only the case in 26 %.

During the last 40 years, therefore, the period of the menarche has gradually become earlier, and how much earlier can be learned from both the following averages. The average menarche of the persons worked out in Table I (fig. 1, curve *A*) of whom the greater quantity was born between 1897 and 1906, is 13 years, 9 months, 15 days; while the mean age of the first menstruation in the persons born before 1880 (fig. 1, curve *B*) is 15 years, 3 months, and 20 days. From this it follows that in the last decades the menarche arrives a year and a half earlier than formerly.

I must point out, in passing, that the last mentioned average more resembles those found in literature regarding the West-European population, which depend on investigations of an older date.

A second manner in which the earlier appearance of the menarche has been proved, is the comparison of the age of the menarche in mothers and daughters. I arranged these data in two groups; in the first I collected the data in which the age of the menarche was accurately known, even up to the month, for both mothers and daughters. To this group belong 45 mothers and 71 daughters. The second group contains the data in which only the year could be mentioned; here there are 56 mothers and 82 daughters.

It seems to me of interest to discuss the data of the first group more extensively, as one or two remarks must still be made about them; they may be seen in Table V, in which the data have been arranged according to the menarche-age of the mother.

From this table follows, in the first place, that of 71 daughters the menstruation of 52 begins at a younger age than in the mother, though, as remarked already, also in the older generation

it was not a rare thing for the menses to begin at the early age of 11. The average age of the menarche of the mothers was 14 years, 9 months, and 25 days; and of the daughters 13 years, 7 months, and 1 day, which means that in one generation the menarche has precipitated with fourteen-and-a-half months. That the difference found here is not so great as what we find on comparing the menarche of women born before 1880 with those born about the beginning of this century (one-and-a-half years), can perhaps be explained by the fact that among the former there were persons of a much older age, and the process of precipitation of the menarche is presumably already longer at work.

The appearance of the menarche in the youngest generation, $14\frac{1}{2}$ months earlier than formerly, as found in Table V, almost coincides with the results of the second group of mothers (56) and daughters (82), of which only the year of the menarche could be mentioned. Here the mothers were, on an average, 15 years, 1 month, and 3 days old, and the daughters 13 years, 10 months, and 15 days; that is again a difference of $14\frac{1}{2}$ months.

These results undeniably prove the considerable precipitation of the function of the sexual glands during the last decades; for although the figures of this earlier appearance of the menstruation may vary a little, one can fix the average at about 14 months.

This is a fact of great importance, highly interesting as physiological phenomenon, and of not less great significance from a social and paedagogic point of view. For the appearance of the menarche 14 months earlier, means to say a shortening of childhood with this period, an earlier activation of the sexual sphere in the present generation, compared to the former. Much of what the attentive observer and listener sees and hears in modern social life is explained by this earlier awakening of the consciousness of womanhood. This is, however, not the place to enter into this question further.

Extensive speculations as to the cause of this phenomenon will not be given here; I will restrict myself to a few general remarks. In the individual process of development of woman the first menstruation is an event of more than ordinary significance; with the commencement of sexual maturity far-reaching changes take place in the general physiology of her development. And if this process makes its appearance considerably earlier this must be looked upon as the expression of a hastened process in her development. Now in the first place the question arises: have we to do here with a symptom of an accelerated development in general, or is it an independent phenomenon? Without special investigations this question cannot be

answered. One would have to examine whether other signs of development are accelerated in the phase before the menarche, e.g. the growth, changing of teeth and such like. The developmental phenomena after the menarche cannot be counted of course, for

TABLE V.

Mother	Daughter	Mother	Daughter	Mother	Daughter
9.12	10.3	13.7	13.4	15.6	14.2
	10.5		12.8		12.6
11.6	11.9	13.7	12.7	15.9	11.11
11.8	11.6	13.7	13.1		12.8
11.9	11.10		12.3	15.12	11.10
	11.11	13.8	14.11	16.2	13.11
	15.2	13.10	11.10	16.4	12.11
11.10	14.12		12.12	16.6	16.1
11.10	11.10		11.11	17.1	13.6
12.7	14.10	13.11	13.10		12.8
12.9	10.6	14.1	10.8	17.4	14.9
	12.7		11.11	17.7	16.3
13.1	12.8		15.9		16.6
13.1	15.11		16.11	18.1	13.8
13.2	12.5	14.2	13.11		13.3 (12.12) ¹⁾
	14.9	14.3	12.6		13.9
	16.11	14.4	13.11	18.4	14.2
13.3	11.12	14.5	11.6		13.5
	11.7	15.1	15.2	18.10	16.6
13.4	13.2	15.2	13.3	18.11	15.3
	13.1	15.3	14.4		14.11
	13.12		15.12	19.4	17.8
13.5	11.3	15.6	14.10		17.9
13.6	11.11			19.8	15.4

¹⁾ Grandchild.

then the development also undergoes the influence of the ovarian function. That this latter should have a retarding influence on the growth of the girl is doubtful, considering the fact that the full-grown daughters of the youngest generation generally surpass their mothers in height.

A second question concerns the cause of the phenomenon; is this early appearance of the menarche a reaction on external stimuli, or is it a primary change in the developing process? That we should have to do with a primary biological phenomenon, with the effect of an internal cause, is doubtful. I cannot imagine that an internal factor could, as it were suddenly, so hasten a developmental phenomenon as appears to be the case in the menarche. If this was an individual phenomenon, an exception, this could be possible, but it is a general thing, which makes it necessary to accept some external influences as cause. I will not enter into speculations as to what these are, but will close this part of my communication with a last remark.

The question can be raised whether, in this considerable precipitation of the menarche, one has to do with a phenomenon which falls beyond the limits of normal physiology. I cannot ascribe such a significance to it, and may venture the following idea. I have on purpose often drawn the attention to the fact that in all the groups which I examined (brunettes, blondes, jewesses, older and younger generations), the variability curve of the menarche begins at $10\frac{1}{2}$ years; that is the threshold-age of sexual maturity. In every girl who has passed this age the sexual sphere can be awakened, though in the one it remains latent longer than in the other. The duration of this period of latency is determined by hereditary factors and by external circumstances. While the part determined by the former is an unvariable one, that dependent on external circumstances is on the contrary very variable. It depends on and changes with the external conditions of life, with the mode of living, nature of food, temperature etc. Whether it is advantageous for the individual or not that the sexual sphere is awakened early under the influence of those circumstances, is a question difficult to answer; but its activation after having once crossed the threshold of maturity, falls within the limits of the physiological norm.

The time of activation of the sexual functions is, as just remarked, dependent on hereditary and external factors. The material I have collected enables me to furnish a proof for both influences.

The significance of the hereditary factor has already been shown by comparing the average age of the menarche in blondes (*Homo*

nordicus) and in brunettes (*Homo alpinus*). A still more convincing proof can be drawn from Table V, for this table shows that if the menarche appears at an early age in the mother, this is, on an average, also the case in the daughter. I have on purpose arranged the data in this table according to the age of the mother.

A simple calculation shows us the following: the average age of the menarche of those daughters, whose mothers began to menstruate in the 11th, 12th and 13th year, is 12 years and 10 months; of the mothers whose first menses appeared in the 14th, 15th and 16th year, the daughters were, on an average, 13 years 7 months old, and finally this mean age was 14 years and 11 months in those daughters whose mothers first menstruated in their 17th, 18th, or 19th year. These ages prove that a retarded menarche in the mother is inherited by the daughter.

Among the external factors which are of influence on the menarche, the temperature, as has been remarked already, is regarded as being of great significance. This opinion was, up till now, only grounded on the fact that the menarche arrives at an earlier age in the population of a warmer zone than in that of a colder climate. Now I can prove from my investigation that this external influence can be demonstrated even in the population of our country. I put the question whether the menarche appears with equal frequency in the different months of the year; and it became clear that this is not the case. The frequency-curve of the menarche, arranged according to the months of the year, has a most typical direction, as may be seen from Table VI. In this table the frequency for each month is expressed in percentages of the whole.

TABLE VI.

January. . . . 8.2 %	May 10.8 %	September . . 6.9 %
February 5.— "	June 10.— "	October 6.2 "
March 7.— "	July 9.5 "	November . . . 7.8 "
April 8.8 "	August 10.9 "	December . . . 8.6 "

This table shows that a first menstruation appears more frequently during the warmer months (May, June, July, and Aug.) than during the rest of the year; for the total frequency during these 4 months is 41.3 % to 29.5 %, during the first and 29.7 % during the last 4 months of the year.

The monthly course, however, is somewhat more complicated. Besides the greater frequency during the summer months there is

another rise in December and January. I should feel inclined to explain this monthly difference in the following way: Beginning with February I should like to regard the rapid and regular rise up to May as a reaction on the general climatological factor, the influence of awakening nature, and not so much as an influence of temperature, which seems to me in these months not capable of doubling the frequency in May, compared to what it was in February. I would then be inclined to see an influence of the temperature in the fact that during the actual summer months the frequency remains almost equal to what it was in May. The rise of frequency in December and January can perhaps be looked upon as the result of the artificial higher temperatures to which the organism is subjected.

As has been mentioned in the beginning of this communication, I have also been able to collect the data of 165 Jewesses, referring to the age of the menarche. Naturally these almost entirely relate to inhabitants of large towns. The following Table VII gives a survey of the frequency, according to the age of the individual, in absolute figures and in relative percentages, which are made clear by curve *A* in fig. 2.

TABLE VII.

Age	Number	Percentage	Age	Number	Percentage
9 year	1		14 year	30	18.1
10 "	3	1.8	15 "	17	10.3
11 "	20	12.1	16 "	9	5.4
12 "	43	26.—	17 "	2	1.2
13 "	39	23.6	18 "	1	

The following remark must be made with regard to this Table. In the 3 cases arranged under the 10th year, the first menses appeared in the second half of this age (10 years, 7 months; 10 years, 9 months; and 10 years, 11 months). The variation curve of the menarche begins, therefore, in the Jewish girls at the same age as in the non-Jewish. It is true there was one case in which the menarche already began at the age of 9 years, but this case (9 years 1 month), is separated by an interval of a year and a half from the following, and must therefore be regarded as a sign of abnormal precocity. For the Jewish race also, therefore, the middle of the 10th year counts as the threshold of sexual maturity. I would again

emphasize the fact that we have been able to demonstrate this age in different groups. In this manner a criterion has been given to determine in each separate case whether one has to do with a real premature development, or with a normal, though perhaps rapid one. A menarche after the age of ten and a half years is a normal event. As far as the threshold-age of maturity is concerned there is no difference between the Jewish and the non-Jewish girls. And yet there is a difference, viz. the greater frequency of the menarche immediately after the threshold has been crossed, so that before the age of 12 the sexual function has begun in 40 % of the Jewish girls compared to 30 % in the non-Jewish blondes, and 18 % in the brunettes.

It is very curious that after this rapid rise in the variability curve, through which the top is already reached at the age of 12, the variation line descends very slowly. Next to a group with accelerated sexual development comes a second with a retarded one. The result is, of course, that the average age of the menarche in Jewish girls is not much earlier than in non-Jewish individuals; for among the blondes I found a mean age of 13 years, 5 months, and 17 days, while for the Jewish girls the average was 13 years, 3 months, and 24 days.

The averred precocity of the Jewish girls compared with the rest of the population, seems, therefore, not to exist, for the slight difference which can be discerned by the above methods, is sufficiently explained by the fact, that the data of the Jewesses, with the exception of a few, refer to inhabitants of towns. I can, therefore, on the ground of my investigation, agree with FISHBERG's conclusion that precocity is not a characteristic of the Jewish race.¹⁾

¹⁾ M. FISHBERG. "Die Rassenmerkmale der Juden." München 1913.

